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MODERN MILITARY ENGINEERING.*

BY

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MILITARY engineering may be defined as the art of so altering the theatre of war as to increase its strategic, tactical and logistic value. Strategy being the art of so directing campaigns as to gain maximum results from success while risking least harm in failure—Tactics the art of winning the battles required by strategy—Logistics the art of creating, training, transporting and maintaining the forces of war. The demand for it is evident throughout the fabric of military organization, from the front line elements in active contact with the enemy where military discipline and combat skill are paramount, thence, in a great war, through the vast communications zone or service of supply where the immediate needs of the fighting troops are cared for and where the military engineer does the bulk of his work, and finally in the heart of the nation itself, whence come all the elements of the country's military strength and where uninterrupted production is the first requirement. Military engineering is dependent vitally both on men and material. In the communications zone, military experience and discipline as well as technical ability are needed to provide all the utilities, communications and establishments required for the immediate support, maintenance and

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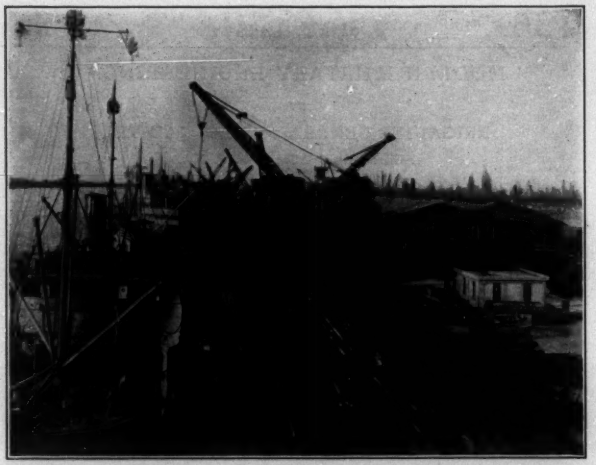
training of the field forces. Everything is fitted to the military program. Here are laid the foundations of all large effort. All material is here collected and made immediately available. Strategic concentrations of supplies, transportation and hospitalization, and all the stupendous construction effort involved, give the military engineer his largest task in war. The popular rôle of the engineer is, however, that of the pioneer soldier, serving

FIG. 1.



alongside the doughboy or the gunner, helping them in moving forward or in stopping the enemy, giving them roads and rail service, shelter and water, information through maps and aid through scientific devices. Modern military engineering embraces all these phases of work. It must be up-to-date, using the latest in science and even sometimes leading science. But while it is essentially modern, it is not new. It antedates history. Permit a foreword as to its development.

Back through the centuries of struggle and progress, we find the engineer performing for his commander, his troops, his strongholds, his cities, his people and his realm the same character of service we are considering to-day. Six hundred years before

the Christian era, the great fortified cities of Persia were connected with the empire's capitol by improved roads. How long before had the art of engineering served mankind, the members of this learned society can no doubt estimate better than I. But we all know that since then, great struggles have often hinged on fortifications; how the very existence of Rome depended upon her great walls which the otherwise victorious Hannibal, genius of war, could not assail; how the great highways that led to

FIG. 2.

Rome, bound that empire of law together; how Caesar built bridges, roads and engines of war to conquer Western Europe and how he saved his army and himself from destruction at Alesia by the ingenious use of field fortifications; how the walled strength of Constantinople held the Mohammedan in check for centuries until the peoples of Europe had awakened from their dark ages and were ready to take up the struggle; how, during these mediæval times, learning and culture and the arts were preserved behind walls which protected their people from the raids of robbers, barbarians or rival neighbors. With the use of gun powder, the engineer developed his plans and methods further to resist attack and strengthen the defender. His walls were more strongly faced to meet the improvement of battering rams, catapults and finally cannon. Here and always the engineer has been confronted by the question of economy; solid masonry

would have solved his problem for centuries, but even the richest cities could not afford the cost. So the stone-veneered walls of the ancients were standard until mechanical means of breaching them demanded provision for a more active defence. Then came flanking towers to permit their archers to shoot along the face of the wall attacked and, on the tops of the walls, other shooting positions for the defenders. The ditch in front came first as a borrow-pit during the wall's construction, but its value in impeding the approach of the attacker, especially if filled with

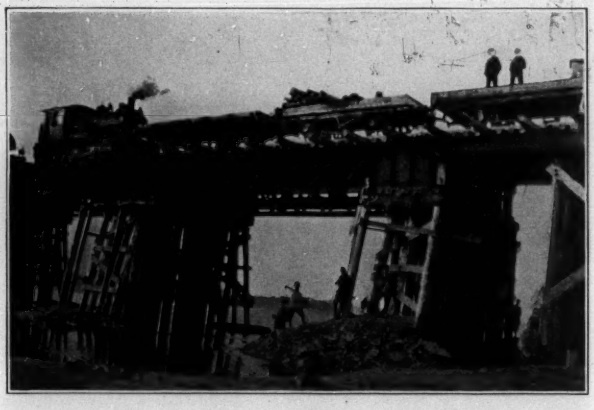
FIG. 3.

water, made its adoption general. The application of the mechanical arts in engines of war, and in methods of siegecraft, was brought to such a stage of perfection by the Romans that their fortifications designed to resist such attack remained practically standard until cannon became able to throw heavy missiles with accuracy at a longer range. To meet this new increased power of attack, the engineer then literally turned his walls inside out, put the earth in front of his masonry, lowered the height of the wall and smoothed the protecting soil out over a sloping glacis which the defenders could sweep with their fire. The ditch was preserved to stop the assault and its flank defence was solved by Vauban, and contemporary engineers, through the bastion system of outline so that every face of the ditch was swept by fire from another face. This general solution sufficed for several centuries and was used in our own coast defences until the coming of rifled cannon and armored ships. Fortifications against ships came along with the age of gun powder, but developed slowly because of the relatively feeble nature of naval attack in that

wooden ships could not mount siege cannon comparable with those employed on land.

How America has profited and prospered through the art of engineering is generally recognized. The value of military engineering in her early growth, however, may not be realized. But for the stockades and blockhouses of the first settlements, the colonists would have been soon wiped out. The surveys of the great western wilderness and the opening of all routes of travel

FIG. 4.



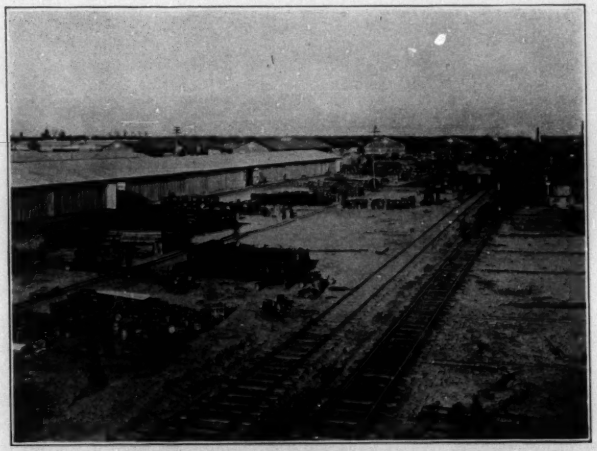
were made by military men. But for our fortifications on the Hudson, Britain would have cut the colonies in two at a critical time and, with the union of Clinton's troops from New York with Burgoyne's from Canada, the American victory at Saratoga, which gave Franklin the lever he needed to bring France to our aid, might have been turned into disaster for our hopes of independence.

The modern period of fortification, and indeed of military engineering, dates from the time of our own Civil War. During that general period, important developments were taking place. The first battle of Bull Run was decided by the arrival of Confederate reinforcements brought over from the Shenandoah Valley by railroad. Thereafter in the movement and supply of troops, railroads played a vital rôle throughout the war. This

forecast the general European adoption of the practice in military concentrations. In the twinkling of an eye, the *Monitor* and the *Merrimac* made all unarmored ships obsolete and placed a new demand on the designer of seacraft defences.

The deadly accuracy of rifle fire was met with hasty breastworks and temporary fortifications of such general use that, by the end of the war, infantry soldiers valued their intrenching tools second only to their rifles. It was during this struggle

FIG. 5.



that wire was first used as an obstacle. A good example of extensive fortification works on the new plan were the defences of Washington: A series of some sixty-eight separate forts or redoubts surrounding the city at such a distance as to protect the capital from bombardment. These defences twice saved Washington and fulfilled their purpose in that they were recognized as too strong for attack save by prolonged siege operations.

American seacoast defences have consistently withstood naval attack and the types developed at the close of the last century (concrete emplacements for disappearing guns) were the most efficient in their time. European practice of mounting seacoast guns in turrets has been used by us only in cases where lack of

space prevented the building of concrete emplacements faced with wide earthen parapets. The present practice, due to the extremely long ranges of high-powered guns beyond accurate observation, omits the heavy protecting parapet and disperses the guns mounted so as to use high-angle, all around fire. Concealment of batteries by dispersion and camouflage is an element of the present doctrine of seacoast defence.

European use and misuse of fortifications during the past fifty years well illustrates the military principles involved. Forti-

FIG. 6.

fications, although conserving the defender's strength, do not by themselves bring victory. Decisive results are obtained only by assuming the offensive. But the superior strength required for the attack at a critical point is made possible by conservation of men and material at other points where the employment of fortification makes such reduction of strength possible. Fortifications are also extremely useful as delaying elements in campaigns. Strategically placed along frontiers, covering lines of approach, they give their armies time for mobilization and concentration. Thus the fortresses of Northern and Eastern France were avoided by the Germans who preferred to violate Belgium's neutrality in the advance against Paris during 1914. Belgium's forts, although practically obsolete in that their guns were outranged by the huge German field pieces, nevertheless so delayed the advance that the British Expeditionary Force and French

reserves were able to meet the invasion and, thanks partly to the influence of the Paris fortifications behind which the Sixth Army was thrown together for the counter-attack, finally defeated the Germans on the Marne. Thus repulsed, the invaders dug in on a line they could hold with fewer men while releasing troops urgently needed elsewhere. Field fortification and siege methods dominated the character of the war on the Western Front for years and until the final breaking through. The successful defence

FIG. 7.

of the forts around Verdun and the maintenance of that single supply artery—the sacred Road—formed a glorious page in the history of French arms and gave the raw British troops their chance to train and take over their share of the task. These are outstanding examples of proper use. On the other hand, disaster in 1870 came to France when two of her generals let their field armies be driven into fortifications where they could neither be properly employed nor adequately fed.

Thus has the art of military engineering come down through history. The profession is an ancient and honorable one. Time sweeps on, methods change to meet new conditions, but, as in the days of Pharaoh so anywhere in the world to-day, the essential elements of the engineers' task can be grouped under three main headings: Time, material, and personnel. If there were no restrictions on any of these elements, the solution would be simple.

In war, however, time is short and materials are usually both insufficient and inadequate where needed. These deficiencies, on the other hand, can be largely compensated by the relative abundance of excellent personnel, if properly organized and controlled. Leadership—experienced, sound, resourceful leadership is essential in the military engineer. When emergencies arise there is little time to study theory and to ponder over its proper application to the case at hand. Instinctive reaction, prompt decision and

FIG. 8.

energetic execution of a proper plan are demanded. War is a great school and develops many leaders—but without initial leadership, few would be able to graduate if, indeed, they survived the disastrous course of instruction.

Common sense would tell us, even if history failed to do so, that efficient engineering leadership in war demands a mind trained to think as a soldier. All effort is bent to fulfil a military mission. A clear concept of this mission is therefore vital. Unforeseen events will arise, changing the mission, often without opportunity to obtain new instructions. When the engineer soldier is under fire he must work on without opportunity to hit back. Much of his work is along highways and railroads which he must maintain, frequently rebuild, and sometimes operate. He must keep the traffic moving. He sees his countrymen going forward for exciting service or returning for rest while he toils

on. Is it any wonder that when he is occasionally allowed to fight he does so with marked success? The leader must know his job to handle such engineers, especially the company and regimental officers who directly control the men. These officers, under our policy of a citizen army, will be, as they were in France, keen young civil engineers, competent, intelligent and full of energy. Inspired to a high sense of duty in the realization of the vital mission they are performing, convinced that their own leader knows his job as a soldier and engineer, their exalted morale

FIG. 9.

will reach the private with the pick and shovel, "every blow of the pick will be a blow to the foe." Every shovel full of dirt will be one more for the enemy's grave.

Important as is the military engineer's contribution in war, it is by no means his only service. Until relatively recent times, most engineers were military men and, while much of their work during peacetime was designed for probable war use later, nevertheless civilization and human progress profited thereby.

Washington, originally a surveyor and an engineer of no mean ability, appreciated the value of this art and employed his engineers—foreign volunteer patriots as well as Americans—to full advantage. It was he who early saw the wisdom of Hamilton's far-sighted plan to establish a permanent Corps of Engineers along with the Military Academy at West Point, and the Academy continued as part of the Corps of Engineers until after the close of the Civil War. For the first third of the nineteenth century it provided practically the only source of skilled surveyors and

construction engineers. These men, in addition to their military duties and fortification work, built and operated the first railroads; surveyed the important trans-continental routes as well as great areas to the West and ran out State lines. Waterway improvement, which the Corps of Engineers started by building the Chesapeake and Ohio Canal and the old Erie Canal, has been carried on to the present time. Those familiar with American harbor improvements along both seaboards and on the Gulf, as

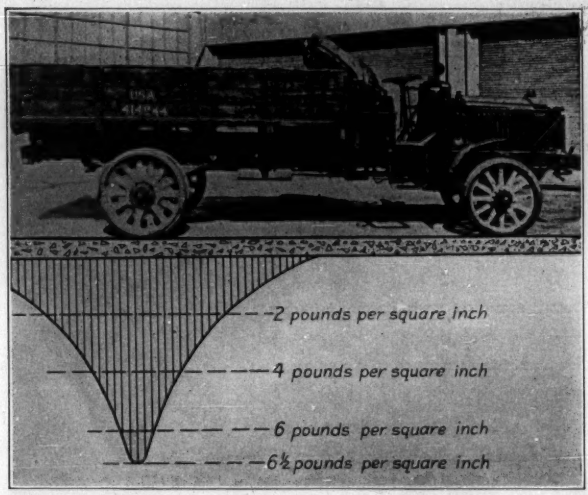
FIG. 10.

well as the navigation opened up on the Great Lakes and some of our inland rivers, know what value the United States has derived from her military engineers.

How does all this work react on the military engineer and how does it affect national defence? By 1812, only a handful of graduates from the Military Academy had joined, as junior officers, the small regular army whose troops bore themselves with credit during those dark days of disaster and defeat. In the war with Mexico, however, the situation had changed. General Scott, himself not a graduate, credited the Military Academy with having made our rapid victory possible through the services of its young graduates. Not a route was taken nor an attack ordered

during Scott's campaign until engineer reconnaissance had been made. The historian, Steele, in his authentic work on American Campaigns, says "truly did the Military Academy repay its cost to the nation in the work of those young graduates in this single campaign." In the four years' struggle for the Union, the services rendered by engineer officers were brilliantly con-

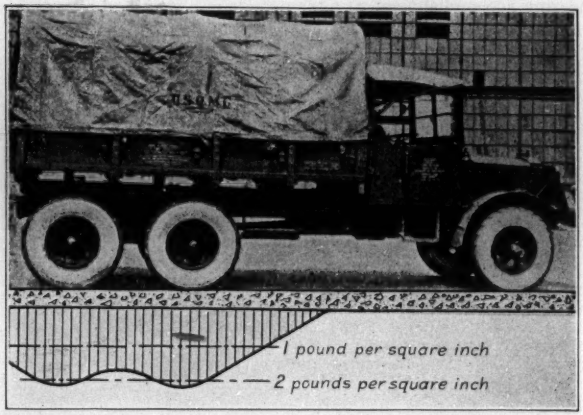
FIG. 11.



spicuous. Not only were the strictly engineering phases of the struggle ably handled, but the actual command of the field forces on both sides fell frequently to former engineer officers. Over forty held the rank of general officer in command of troops. Ten commanded Army Corps and eight were given charge of independent field armies. McClellan's genius raised, trained and equipped the great Northern Army of the Potomac. At the high tide of battle, the turning point of the war—Gettysburg—both sides were commanded by engineers, George G. Meade and Robert E. Lee, while the northern chief engineer, Warren, secured the victory by his prompt assumption of authority in ordering the key position occupied.

Since the Civil War, the country has many times drawn on this reservoir of leadership. The best known case perhaps, at least until the recent emergency, was that of the Panama Canal. It was my privilege to put some four years on that work under those great engineers: Goethals, Hodges, Sibert and Gaillard. They were sound in organization and in technique and they

FIG. 12.



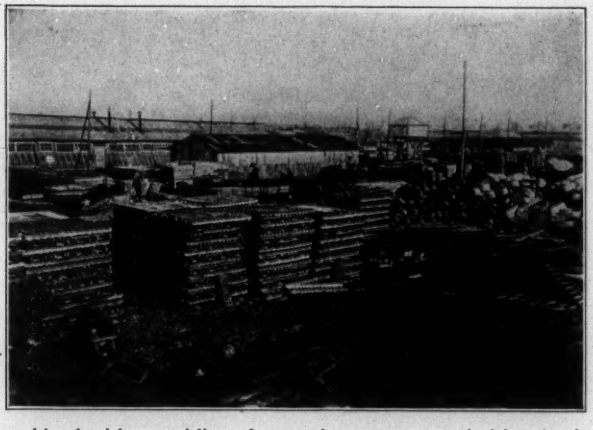
inspired an esprit de corps throughout the vast civilian force which made failure impossible.

After all, these satisfactory results of emergency service are hardly surprising when we stop to analyze the system under which American engineer officers are trained. They are first of all soldiers with a clear sense of duty and a simple code of honor. They keep in touch with the military side of their profession. On the other hand, they are grounded in the theory of engineering and are developed by actual practice in concrete problems of no mean magnitude. In river and harbor improvement, as in perhaps no other branch of the profession, the engineer must match his ingenuity against the uncertain forces of nature and is thus given opportunity to develop the important traits of resourcefulness and decision.

Less conspicuously perhaps than in the Civil War, this same

principle was demonstrated in the recent emergency. During our year and a half of participation in the World War, thirty-five officers, who had held engineer commissions, served in the grade of general officer. Although several commanded divisions, and many led brigades the outstanding contribution of the corps was probably in engineering. The task of building the American Service of Supply in France has been described as an engineering accomplishment of a magnitude in extent and importance,

FIG. 13.



combined with a rapidity of execution, unsurpassed either in the history of war or of civilization. Most of the physical work was done by thousands of civil engineers, contractors and others temporarily wearing the country's uniform and actuated by an exalted spirit of patriotism and sacrifice. They worked under the leadership of our military Corps of Engineers. This work was one of the vital elements that made victory possible and any appreciable failure on their part would have spelled disaster to our fighting forces. It is not an exaggeration to say that but for this accomplishment, the war could not have been won in the fall of 1918.

How utilitarian is the present-day service of our engineer officers can perhaps best be shown by listing the duties now

being performed by them—living examples of modern military engineering:

The Chief-of-Engineers;
The present Chief-of-Air-Service;
The Commanding General of the American Forces in China;
The present Chief of the Chemical Warfare Service;
The Governor of the Panama Canal and his Director of Maintenance;

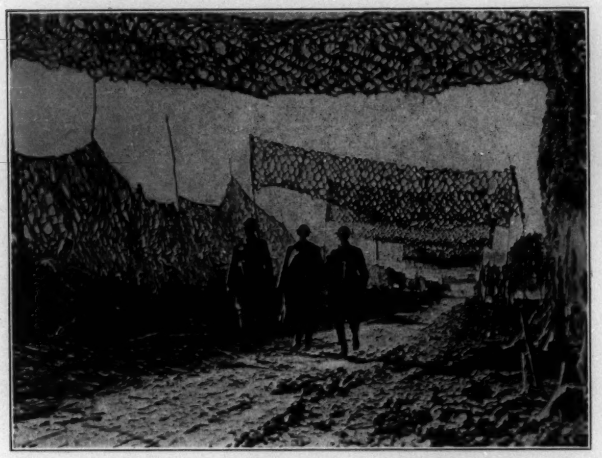
FIG. 14.

The Chief Engineer of the Federal Power Commission;
The Military Aide to the President;
The American Representatives on the Joint Engineering Board for the St. Lawrence Waterway;
The Commander of the American Brigade in the Philippines;
Until recently, our Military Attachés in Pekin, London, and Havana;
The Engineer Commissioner, District of Columbia;
The Director of the Bureau of Printing and Engraving;
The President of the Alaskan Road Commission;
38 officers serving on the faculties of civilian universities, colleges and schools;
21 officers serving on the faculty of the U. S. Military Academy at West Point;
17 officers serving as instructors of the National Guard;
92 officers engaged on river and harbor improvement;
55 officers under instruction as students;
267 officers are serving with troops, Engineers, General Staff, and other branches.

These officers constitute a readily available reservoir of engineering ability.

This is our American conception of modern military engineering. In actual practice throughout the A.E.F., engineer activities covered a very wide field. The bulk of the work was characteristically orthodox and prosaic—hard driving labor—but a few glimpses at key points mixed with certain of the new developments

FIG. 15.



and specialties, may serve to remind us what modern military engineering meant in France, and may mean to us in the future.

General Pershing, in his final report, characterizes the construction work carried out by his engineer troops as among the most notable achievements of the American Expeditionary Forces. The chief projects were port facilities including docks, railroads, warehouses, hospitals, barracks, and stables—planned for four million men and carried on coincident with the growth of the Expeditionary Forces. For example:

The Bassens Docks (Fig. 1) were built by American Engineers as a base port near Bordeaux providing berths for ten vessels and so equipped with modern unloading facilities that during the critical three months' period, a daily average of 3700 tons

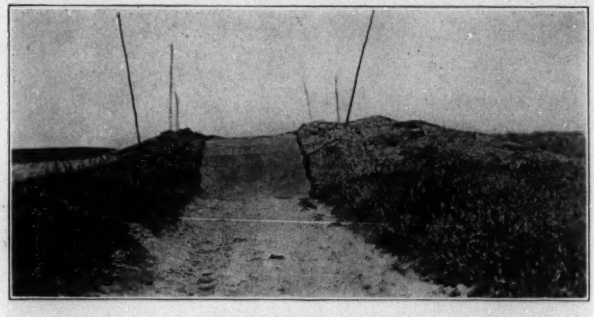
was handled. In all, eighty-nine ship berths were built or acquired from the French.

Illustrating the next link in the project—La Rochelle Yards (Fig. 2) were used for the assembling of U. S. standard railroad equipment.

Fig. 3 shows a view of *St. Sulpice* railroad yards and warehouses—a Base Section installation.

The Nevers Cut-off.—In connecting the base sections with the advance areas certain railway main-line improvements were

FIG. 16.



demanded. In by-passing the rail centre of Nevers with a 6-mile cut-off (Fig. 4), several hours were saved in transporting men and materials. The project, completed in October, 1918—in four months' time—required 190,000 cubic yards of cut, 414,000 yards of fill and double-tracked bridge 2190 feet long over the Loire River. In all, some 1053 miles of standard gauge track were laid in France by American Engineers.

At Gievres there was built a general intermediate storage depot in the intermediate section with capacity for supplying a million men for thirty days. The project covered twelve square miles. (Fig. 5.)

The hospital project at Mars (Fig. 6) for " 20,000 beds " was only one of four, while many of " 10,000 beds " and smaller were built, each a complete municipality with road, water sewerage and lighting facilities.

These are but typical of the S.O.S. construction project, the

size of which is indicated by its twenty-two million square feet of covered storage space which protected forty-five days' reserve supply for 4,240,000 men and provided new hospital space for 141,000 beds in addition to that for 139,000 beds in French buildings; refrigeration capacity for forty-four million pounds of meat and a daily ice supply of 1000 tons. If the 17,120 barrack buildings were placed end to end, they would have extended 285 miles, or from Philadelphia to Norfolk. Remount space was

FIG. 17.

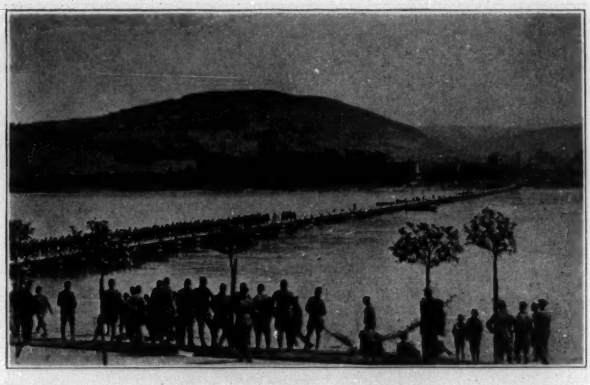
provided for 39,000 animals and veterinary hospital accommodations for 23,000. Mechanical bakeries were capable of turning out 800,000 pounds of bread daily. Nine engineer supply depots received and handled three and a third million tons of engineer material. Seven cement mills turned out 313,000 barrels of Portland cement in five months and over a hundred miles of concrete pipe were made for A.E.F. use.

One of the eighty-one mills operated by the A.E.F. Forestry Service is shown in Fig. 7. These mills put out 218 million feet B. M. of lumber, four million railroad gauge ties; 1,800,000 poles and props; 39,000 pieces of piling and fuel wood, which, if

corded, would extend 375 miles or from Philadelphia to the Canadian Border near Lake Champlain.

Connecting up with broad gauge supply lines and reaching forward to the troop distribution points in the active zone of the Armies, the light railway service (Fig. 8) had 2240 kilometres of narrow gauge track in operation at the time of the Armistice. Three-fourths of this had been captured from the Germans and the remainder built or rebuilt by American Engineers. The net

FIG. 18.



daily tonnage carried by this service during October, 1918, was 8100 tons. After the Armistice this service of light railways and roads employed 100,000 troops on 7000 miles of road work.

The construction and maintenance of highways was performed by engineer troops in all parts of the American Sector from the base-ports through the divisional areas. The destructive effect of shell-fire at the front was, if anything, less than the wear and tear of the heavily loaded trucks which, during the prevailing wet weather, rapidly wore away the macadam road surfaces.

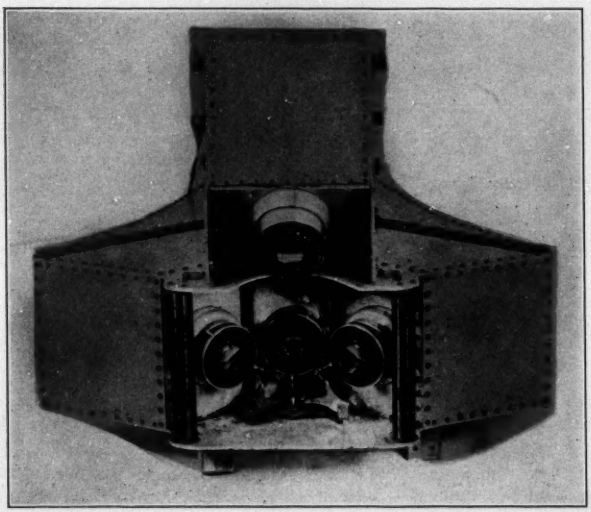
The *Remonville-Barricourt Road* was the main supply artery of our Fifth Army Corps which broke through the German line for ten kilometres on November 1st and inspired the remark from Marshal Foch, "La Guerre est finis."

The Highway near Malancourt (Fig. 9) shows the character of terrain across No Man's Land where this main supply road was

rebuilt and maintained (Fig. 10). The measure of repair demanded is best understood from the amount of rock required. In the First American Army alone, the Engineers received and placed an average of 2400 tons of rock daily. During the last eleven days of fighting, double that amount was required. The hauling of this rock was in itself a severe tax on the highway system.

A new type of motor transportation, developed as the result

FIG. 19.



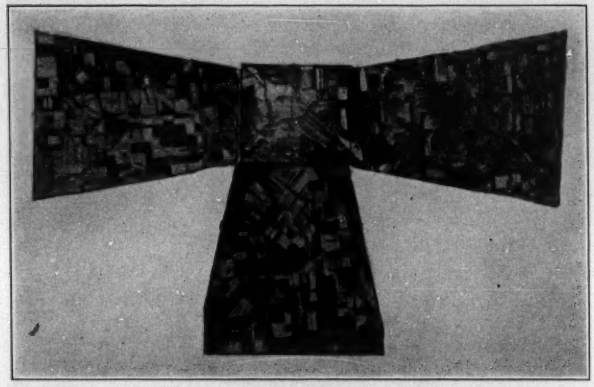
of World War experience, should alleviate the engineer's task of road maintenance. Even with increased speed, the unit pressures and impact are below those of the present standard equipment. (Figs. 11 and 12.)

The final distribution of engineer supplies to the combat troops was performed by divisional engineers from "dumps" as shown in Fig. 13. Twenty-five thousand tons were required for the St. Mihiel operation and 50,000 for the Argonne. These included 10,000 miles of wire, six million sand bags, 96,000

picks and shovels, 250 miles of railroad track delivered and installed.

Water supply for the field armies was also handled by the Engineers. In the Argonne, 1,200,000 gallons were daily required for men, animals, locomotives and trucks. Of this, half a million gallons were chlorinated daily. This purification service was handled by mobile sterilab units (Fig. 14), operating at troop supply points for distribution to the horse-drawn carts of each

FIG. 20.



battalion. This supply was augmented by tank trucks and tank cars moved by rail.

Camouflage in our Army is supervised by the Engineers who supply all material. In France our A.E.F. camouflage factory near Dijon had a monthly output valued at a million and a half dollars, involving three million square yards of burlap, 800 tons of paint and glue, a million and a half feet of rope and two million square yards of chicken wire. This was used to conceal observation points, posts or commands, dumps and nearly six thousand separate gun positions. The importance of this work was expressed by the French in: "A battery seen (vue) is a battery lost (perdue)." (Figs. 15 and 16.)

Bridging operations on an extensive scale were demanded throughout the American sector for railroads, heavy and light,

for motor and animal-drawn transportation and for troops crossing streams under fire. Our Engineers solved their various problems by appropriate construction, varying from heavy girder and trestle bridges, through the lighter open truss of standard design to the floating types for front line work (Figs. 17 and 18). Here American experience dating from the Civil War proved of

FIG. 21.

great value, as the only pontoon equipment available was of foreign manufacture. It was, however, sufficiently similar to our type to permit our combat engineers to handle it even for night operations. Bridge work during the St. Mihiel operation and several forced crossings of the Meuse River during the latter stages of the Argonne fighting were comparable with the best work in the Civil War. To provide a light portable bridge for quick crossing by infantry, the Lampert type was developed and put

into operation. It is similar in design, although much lighter than the folding canvas pontoon bridge developed for American Cavalry in the Civil War. The latest improvement on this design is the use of Kapok as the floating element in support of the light bridge.

The magnitude of map requirements for modern war is expressed in terms of the fifty million maps used by the Allied Armies during the last emergency. To provide the American

FIG. 22.

Expeditionary Forces with its maps, the Engineers established at Langres, near Chaumont, a base map reproduction plant of modern machinery which produced during 1918, some five million maps. In addition to this base plant, American ingenuity set up a mobile map reproduction train of motor trucks which moved forward in advance of the First Army Headquarters and provided an immediate supply of the latest map information to the troops actually engaged in the fighting. In France, American methods of obtaining topographic information as well as of reproducing maps were proved equal, if not superior, to the British, French or German. As far as possible, use was made of aeroplane photographs, but time was too short and the immediate demands too severe to permit of much development along

this line. However, Major Bagley, an Engineer Officer, started work in France and has now produced a multi-chambered camera (Fig. 19) by means of which topographic information can be obtained from aeroplane photographs. The wing views, as shown, provide means of adjusting a series of photographs on each other and upon the geodetic control established on the ground. (Fig. 20.)

The latest development in topographic map portrayal is

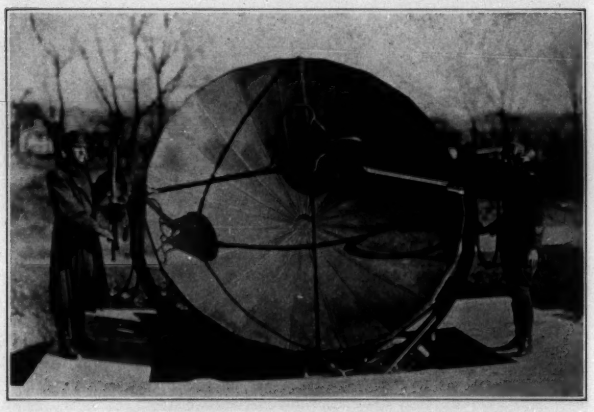
FIG. 23.

shaded relief. The natural and yet scientifically accurate appearance is obtained by photographing a true model of the relief vertically lighted and then accurately superimposing the shadows, by half-tone process, on the regular topographic maps. (Fig. 21.) This development by the Engineer Reproduction Plant is considered an important advance in the art and science of map making.

As an adjunct to military mapping, the service of flash and sound ranging (Fig. 22) was an important specialty handled by the Engineers. The methods found in use by the British and French were taken over and improved by the best American

talent obtainable with a result that enemy gun position, although concealed from aeroplane observation, was consistently located with an accuracy well within the normal dispersion of artillery fire. Flash ranging, where two or more observers could see the flash of the firing artillery, was, of course, most accurate. On the other hand, in the majority of cases, the guns were entirely hidden from view. However, by the accurately timed reception of the sound wave at several carefully located stations all recorded elec-

FIG. 24.



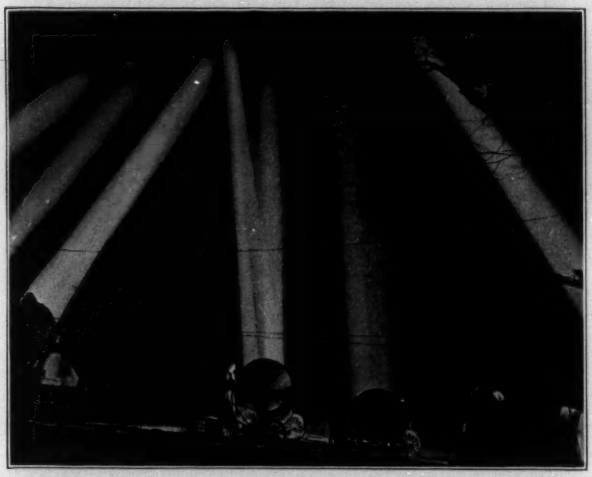
trically on a single sheet of smoked paper, enemy guns, firing singly for registration could be easily computed.

Searchlight development had been going on for years as an adjunct to American seacoast defence, but the advent of the aeroplane and the need of defence against its night operations made the long-range searchlight invaluable in France. Back of the American lines, a lighted zone, along the lanes of the enemy's habitual approach by aeroplane, was maintained each night extending over an area from 350 to 450 sq. km. Enemy planes were "picked up" by the searchlight beam so that the gunners or the American pursuit planes could locate them. In most cases, however, the enemy plane, once illuminated, would promptly turn back. To assist in locating the plane from the

hum of its engine, various devices were developed, such as the one shown in Fig. 23.

The reception of the sound wave is so carefully tuned that the direction of the plane can be very accurately determined. (Fig. 24.) In addition to this electrical work, the Engineers with the field armies, maintained and operated some 250 electric

FIG. 25.



light plants for depots and various headquarters. A battery of searchlights in operation is shown in Fig. 25.

It is impossible here to give more than mere mention to the tremendous expenditures of time and labor given to field fortification on the Western Front—work required constantly by all troops, especially the Infantry, Artillery and Engineers. The latter were given the more difficult tasks, mining, deep structures and construction of common posts while supervising and helping lay out the work for the Infantry. Tools and all material such as wire, revetment, lumber and "duck boards" were furnished by the Engineers. It is unnecessary to point out that such warfare was a highly specialized development, due to stabilization and only gave way to mobile operations on the Western

Front during 1918. Although our troops had relatively little service in the typical trench warfare, its fundamentals are well understood by Americans and a practical adaptation will certainly be available to us in any similar emergency that may confront us.

The most effective obstacle used in impeding the advance of the troops, so that they could be held under fire, was the interwoven mass of barbed wire found in front of every trench. (Fig. 26.)

Engineers furnish this wire, and sometimes put it up or help

FIG. 26.

the Infantry in so doing. But in advancing during attack the pioneer troops are given the reverse mission of opening lanes for the Infantry. The Artillery can assist greatly in concentrating its fire on critical points, but the accuracy of modern gun fire cannot be relied upon to open up paths for an extensive advance. One demolition device is a type of explosive known as the Bangelore torpedo, which like a jointed fishing-pole is pushed through the wire and exploded. This is supplemented by wire cutters and sometimes by throwing a heavy net carpet over the top of the remaining wire. This is perhaps the engineer soldiers' most dangerous service, because its work is frequently subjected to heavy concentrations of fire.

Such in general was modern military engineering in France.

Peacetime work by the Corps of Engineers, so essential to training for war work, extends over the whole United States as well as in the outlying territories.

Only a few of the characteristic examples in this work can be shown in our limited time to-day, but let us consider some key points:

The development of America's most important seaport has been possible only through the widening and deepening of its channels. Starting in New York Harbor with a maximum allow-

FIG. 27.

able depth of sixteen feet through tortuous channels, safe passage is now provided for the largest sized trans-Atlantic liners and the capital ships of the Navy. Some parts of this work in the inner harbor have required subaqueous dredging of rock and even subterranean mining. The bulk of the excavation, however, has been in the outer bars where the Corps of Engineers has developed an efficient type of sea-going hopper dredge which maintains the channels at the proper width and depth at low cost.

Our latest development is a Diesel engine dredge which generates its own electrical power for propulsion, dredging, steering and all conveniences of the crew. This is the latest thing in electrically driven marine construction.

An interesting example of special work given to the Engineers was the raising of the battleship *Maine*. The problem required

the unwatering of the old vessel for expert inspection in order to determine, if possible, the cause of her sinking in 1898.

From the standpoint of commercial tonnage, the development of navigation channels connecting our inland lakes, and their many harbors, is on a par with the projects for New York and other harbors.

Duluth Harbor alone handles from thirty to fifty odd million tons of freight annually, valued roughly at three to five hundred

FIG. 28.

million dollars. Over 80 per cent. of the incoming freight is coal and even larger percentage of shipments is iron ore. The extent of tonnage at other Lake Superior ports is shown in the great volume of traffic passing the Sault Ste. Marie—fifty to eighty million tons annually, valued at approximately one billion dollars. While the bulk of this traffic moves through Lakes Huron and Erie, part is with Milwaukee, Chicago and Lake Michigan ports. About 80 per cent. is carried in deep-draft vessels which, however, are limited to twenty feet due to existing channels and water levels.

Through our own American improvements, the harbors on the four upper lakes are connected for approximately twenty-foot navigation. The Canadian government also has locks at Sault Ste. Marie and the fourteen-foot Welland Canal connecting

Lakes Erie and Ontario. Vessels of light draft can load in the Great Lakes for trans-oceanic shipments, completing their loading at Montreal. The value of the proposed deep waterway *via* the St. Lawrence and of the great hydro-electric power capable of simultaneous development are under consideration.

While lake navigation in the main is less difficult than open sea travel, due partly to the excellence of our Lake Survey Charts and pilot information, violent storms and winter ice make harbors

FIG. 29.

of refuge necessary. To meet this demand, an "arrow head" type of break water has been developed and widely used, in which vessels may seek shelter and where the effects of heavy wave action are greatly reduced. (Fig. 27.)

Similar in character to the Soo development is the canal connecting Lake Washington, Seattle's inland harbor, with Puget Sound and the sea. (Fig. 28.) These are good examples of lake improvement.

Our most extensive river improvement is found in the valley of the Mississippi and its main tributaries. With nine-foot navigation being provided between New Orleans, St. Louis, and Pittsburgh, and six-foot channels to St. Paul and also on several

Ohio River tributaries, our inland development bids fair to be the best system of inland waterways in the world.

Navigable depths on the Upper Mississippi are maintained by regularization or confining the channel with wing dams and making the stream maintain its own proper depth by scour. (Fig. 29.) Below Cairo, however, where the Missouri and Ohio waters swell the volume of flow, one problem is to keep the river between its banks even in time of high water. The loss of life and

FIG. 30.

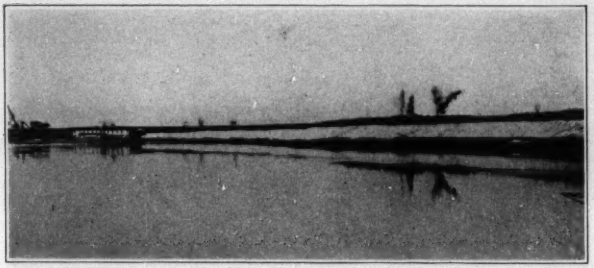
property, not to mention crop destruction, due to floods, in this great valley has been so stupendous as to justify the Federal government in joining in the great task of levee work and bank protection. After years of study and improvement, this problem seems assured of solution and the great river will be fairly safely confined to its high bed and levee topped banks. (Fig. 30.)

The task now remains to hold this advantage by proper bank protection against the river's ceaseless scour. The old standard willow mattress built of fascines is being challenged by a more modern and probably more lasting mattress of articulated concrete blocks for use above the low-water line. (Fig. 31.) The engineering problem presented by the delta of the Mississippi

is one requiring constant attention and sound practice based upon carefully recorded experience.

One of the best examples of river improvement by canalization is found in the Ohio, where successive pools are provided by movable dams of moderate lift for low-water season navigation through amply dimensioned locks. The improvement is well designed to carry the traffic peculiar to the stream. When high water floods out the locks, open river navigation is provided by lowering the dam. Ordinary fluctuations are handled by hydraulic gates of the bear trap type. Construction behind coffer-

FIG. 31.



dams in the low-water season affords excellent training for the young engineers in charge. There are approximately fifty of these dams costing over a million dollars apiece and the project is rapidly approaching completion.

Wilson Dam at Muscle Shoals, concerning the future of which there is considerable public interest, affords an interesting construction problem for our Corps of Engineers.

When finished, this dam and power-house will not only provide a large and useful supply of power but will open the river for navigation many miles upstream and form a link in development of the Tennessee River project.

CONCLUSION.

In closing, I may say that we of the military engineers feel that we have much in common with The Franklin Institute. Bearing in mind the old Military Academy, created with our permanent Corps of Engineers, we can draw certain fundamental simliari-

ties with the institution whose centenary we are now observing: Both were pioneers in American scientific practice; both were founded on solid democratic lines; both were dedicated to utilitarian service; both have given hundreds of trained men to work for the nation's progress and advancement; both have endured.

The economy and maximum utilization of material and time practiced by the military engineers in France would have delighted the far-seeing patriot and practical savant whose name and spirit confer luster on your Institute and hover over our relations with our sister republic across the sea.

Synthetic Methanol.—Methanol has had a somewhat dramatic history. Long known only as one of the products of destructive distillation of wood and without important applications, it became, in its crudest form, the means of denaturing alcohol in Great Britain. Allen's "Commercial Organic Analysis" made American chemists familiar with the name but not with the nature of "methylated spirit" so largely prescribed in analytic methods. Later, processes of purification enabled the production of a high-grade article almost absolute, and Dr. Benjamin Ward Richardson, a British physician of much ability and originality, but sometimes rash in his inferences, was led to suggest that in this pure form it would take the place of ethanol and serve as a valuable substitute. The refined product began to appear in quantity under misleading titles such as "Columbian Spirits," "Colonial Spirits," and very soon evidence of its peculiar toxic action on the optic nerve was noted. Numerous sad cases of blindness, even by exposure to its vapor, were reported.

It has always been a question whether the toxic action of methanol is due to the substance itself or to some unrecognized impurity. The ordinary explanation that it oxidizes in the system to formaldehyde, while ethanol becomes carbon dioxide and water, seems to have no positive experimental basis, though it is plausible. Heretofore the industrial source of methanol has been only the distillation of wood, but it appears from recent reports that a synthetic product is now available. This will probably bring new issues into the alcohol problem, for if the synthetic article is free from the toxic action so characteristic of ordinary methanol, a new intoxicant is added to the list and new legislation will be needed. It is, indeed, not likely that the better class of liquor users will resort to methanol, however pure, but a large fraction of the lower class will be brought under its sway.

Some information concerning the method for synthesizing methanol is given in a paper by G. Patart, Inspector-General of the French powder works, in *Chimie et Industrie* (1925, **13**, 179), abstracted in *Ann. Chim. Anal.*, etc. ([2], 1925, **7**, 109), from which the following data are taken. The process is an example of catalysis

under high pressure, which has already shown such great efficiency in connection with the synthesis of ammonia. As usual with French scientific literature, suggestion is made of early French work, when Messrs. Sabatier and Senderens attempted to combine carbon monoxide and hydrogen by the influence of finely divided nickel, but accomplished nothing of importance, because they worked at atmospheric pressure. In 1913 the Badische Anilin und Soda Fabrik, the BASF, now so well known in industrial chemistry, made a number of experiments, obtaining several aliphatic derivatives of low carbon content, but did not pursue the work to definite result. Similarly, Henri Dreyfuss failed with both nickel and platinum sponge as catalysts. Calvert in 1922 claimed to have obtained a good yield of methanol from water-gas and hydrogen, but gave no details of his method. In the same year Patart took out a patent in which it was claimed that carbon monoxide and hydrogen can be combined under the influence of catalysts at a temperature of 300° to 600° under high pressure to form methanol, but his claim was disputed by other workers. In 1923, the BASF took out patents for a process essentially similar, but covering numerous accessory important points, such as purification of the applied gases and use of new catalysts. In consequence of the coöperation of theory and practice which is so characteristic of German industries, a large amount of synthetic methanol was produced, which was at once absorbed in the color industry. French enterprise also developed the synthetic product and a small installation was operated under Patart's methods in 1922. A pressure of from 150 to 250 atmospheres and temperatures from 400° to 420° are employed. The statement is made that the alcohol can be produced at about twenty-five cents per gallon, but this, of course, is on a French labor basis and cannot be safely applied to American manufacture. It is expected that the production will bring methanol into active competition with standard motor fuels, a consummation devoutly to be wished. It is, however, in the color industry that the production of a methanol wholly free from acetone will be of the greatest importance, and the manufacture of formaldehyde will also be materially aided. The reduction in the cost of formaldehyde will be felt in the lowering of the price of the largely used derivatives, such as bakelite. H. L.

Magnetic Work in the Union of Socialistic Soviet Republics. BORIS WEINBERG. (*Terrestrial Mag.*, Dec., 1924.)—The Observatory of Zuja, near Irkutsk, has once more begun to function regularly, that in Nova Zembla, with the exception of short intervals, worked all the previous winter, the Tashkend Observatory will soon have instruments to replace those destroyed and a new observatory is planned for the region of Vladivostok. A beginning has been made in the systematic re-occupation of 116 stations so that a study of secular variation may be conducted. G. F. S.

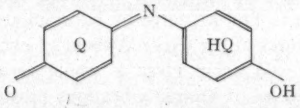
A THEORY OF COLOR PRODUCTION.*†

BY

JULIUS STIEGLITZ, Ph.D., Sc.D., Chem.D.

The University of Chicago.

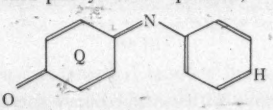
MANY theories have been formulated to account for the occurrence of color in both inorganic and organic compounds. Particular emphasis has been placed on the question of the source of the color of those brilliant, intensely colored organic compounds which are useful as dyes. For about half a century the connection between the occurrence of color in these beautiful dyes and the chemical structure or arrangement of the atoms in their molecules has been well understood. One can recognize in the structure of the molecule of any organic dye the two fundamental *groups of atoms*, the importance of which was first recognized by Otto N. Witt [1] in 1876. They are the *chromophoric* or *color-carrying* group of atoms, and the *auxochromic* or *color-intensifying* group. In the structure of one of the simplest typical dyes, an indophenol $O:C_6H_4:N.C_6H_4OH$, or



Indophenol (I)

the quinoid group Q is the chromophore and the OH group in the hydroquinoid complex HQ is the auxochrome.

Nearly all of these dyes are either basic or acid in character, and a third fundamental factor has been recognized, namely, that the maximum intensity and depth of color of such dyes is very commonly developed through salt formation. To illustrate the three factors, we find phenyl-imido-quinone,



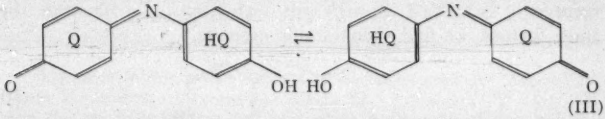
(II)

* Address delivered Wednesday, September 17, 1924, on the occasion of the celebration of the centenary of the founding of The Franklin Institute.

† The theory was first publicly presented in an address before the Minnesota Section of the American Chemical Society in December, 1920 (*cf. J. Amer. Chem. Soc., Proceedings*, **43**, 36). *Cf. Proc. Nat. Acad. Sci.*, ix, 303 (1923).

which contains a chromophore Q but no color-intensifying group, yellow; this is the shallowest of all colors and results from the absorption of the shortest visible wave-lengths of white light. With the introduction of the auxochromic OH group found in the indophenol (1), the color is deepened to red; and by the addition of alkali, we obtain the maximum color depth and intensity for the dye, an indigo blue, through the formation of the sodium salt of the dye.

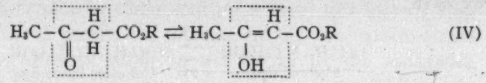
The recognition of this connection between structure and color has formed the scientific basis for the marvellous development of the dye industries in the last half century. But it does not in itself explain color, which is dynamic, the result of the absorption of moving light waves and of the passage of the unabsorbed waves through the dye, if we speak in terms of the wave theory of light. Structure in itself can no more explain the fundamental nature of the absorption than the structures of a piano or of a violin in themselves can explain the production of the tones which they produce and which depend, of course, on the vibration of their strings held in definite restraints. For this reason many efforts have been made to find a source of harmonious vibration in the molecular structures of the dyes: Watson's[2] excellent monograph on constitution and color gives a whole series of interesting theories as to waves of atomic vibrations passing from one end of the dye molecule to the other. The simplest of these theories is the old assumption of a tautomeric shift of the quinoid part of the molecule to the hydroquinoid part, to and fro, with the necessary changes of the valence bonds involved:



(III)

But light waves move with extraordinary speed and these atomic rearrangements of whole molecules appear much too cumbersome to be compatible with so fast a wave motion. In fact, the analogous but much simpler tautomeric change between the two forms of aceto-acetic ester, which was early recognized as being

similar in character to the more complex tautomerism of the dye molecules



(IV)

was found experimentally by Kurt Meyer [3] and by Knorr [4] to be so slow in the absence of catalysts that the cycle Keto → Enol → Keto required for an average molecule from seventeen days (Meyer) to one-half a year (Knorr) at room temperature.

That the vibrating component in the dye molecule must be an electron or electrons, and not an atom or a series of atoms, was finally recognized by such investigators as N. R. Campbell,[4] G. N. Lewis,[5] Baly [8] and others, and there is no doubt that these authors are right in this conclusion. But which electrons of the many in a dye molecule are subject to these vibrations leading to the absorption of components of white light, why such electrons are found in the molecules of a dye and not in colorless compounds and, above all, what the connection is between these electron vibrations and the well-established facts relating color to structure and salt formation, are questions which, so far as I am aware, were not answered.

In the present address, I shall endeavor to develop this fundamental connection and show how simply the demand of modern theory for electron vibrations as the source of absorption fits in with the facts of the color theory connecting color and structure—and I shall endeavor also to show how exactly the same theory explains why we have color in large numbers of inorganic compounds, and why the great majority of inorganic as well as organic substances are colorless. This general theory of color production started from a study of the organic dyes, and was subsequently found to lend itself to colored inorganic compounds. I shall follow the same course here, starting with the question of color of the dyes.

The key to the fundamental relation between electron vibrations and the structure of dye molecules, on the one hand, and the three great factors, the chromophoric, auxochromic and salt-forming groups in these molecules, on the other, is found in a fourth general fact long known as holding for all dyes without exception: By *reduction,* every dye known becomes colorless,

forming the so-called leuco-dye; by *oxidation* of the leuco-dye, the color is restored. This is a universal fact. For indophenol we have:

$$\underset{\text{Colored dye}}{O{:}C_6H_4{:}N.C_6H_4OH} \underset{-2H}{\overset{+2H}{\rightleftharpoons}} \underset{\text{Colorless leuco-dye}}{HOC_6H_4.NH.C_6H_4OH} \qquad (V)$$

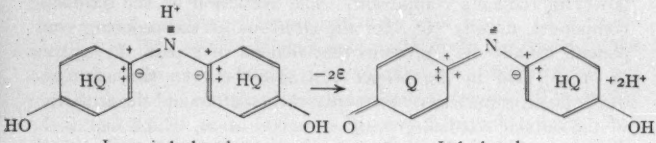
But, fundamentally, reduction is known to consist in the absorption of electrons by atoms, oxidation in the loss of electrons by atoms. This well-known fact of modern atomistics is illustrated by the simple relation between ferrous and ferric salts:

$$Fe^{++} \underset{+\varepsilon}{\overset{-\varepsilon}{\rightleftharpoons}} Fe^{+++} \qquad (VI)$$

All oxidized atoms are invested in turn with oxidizing power, that is, with the power to attract and draw to themselves, and finally to absorb electrons from neighboring atoms. It is in this power that we shall find a fundamental correlation between the two great phenomena, oxidation-reduction and color-production, for both have in common their dependence on the freeing of valence electrons from the ordinary intra-atomic restraints. In the case of oxidation-reduction, this freeing from restraint proceeds to the point of actual transfer of valence electrons from the reducing to the oxidizing atoms, under the influence of the attractive forces of those oxidized atoms; but in the case of color production, valence electrons are freed only sufficiently from intra-atomic restraints by nearby oxidizing atoms to make possible vibrations under the impact of light-waves in the range of visible color and the consequent absorption of the latter.

Let us follow this clue in a specific case to make the thought quite clear. In the colorless leuco-indophenol dye (V) we have a perfectly symmetrical molecule, dioxy-diphenylamine. It is a powerful reducing agent, that is, it gives up electrons easily, being a simple derivative of aminophenol, $H_2NC_6H_4OH$, a strong reducing agent used as a photographic developer. It is closely related, of course, to quinol, HOC_6H_4OH, another well-known photographic developer with strong reducing power. It is clear from the symmetrical structure of the leuco-dye that either half of the molecule could be oxidized, since each half has the characteristic reducing group—NHC_6H_4OH. The oxidation always

involves *the loss of two electrons* from some atom of the molecule and eventually results in the loss of two hydrogen atoms H^+. For reasons which cannot be elaborated upon here, this loss of electrons is considered possible in the case of the two carbon atoms united to the nitrogen atom in the centre of the molecules. If we remove these two electrons from the carbon atom on the left, there remain still two similar electrons in the carbon atom on the right, because we could just as well have decided to consider that side oxidized. We can express these relations graphically as follows:



(VII)

The positive signs indicate positive nuclear charges left on the carbon atoms by the removal of the corresponding valence electrons. Whether we have here complete removal as in the case of a completely polar sodium ion Na^+, or a zinc ion Zn^{++}, or so-called partial polarity as in carbon dioxide $O::\overset{+}{\underset{+}{C}}::O$, with the valence electrons much closer to the oxygen atoms than to the carbon atom, is a matter into which we cannot go at present. That partial but absolutely definite polarity results is the view I personally am inclined to hold. The negative signs $\ominus$ indicate the pairs of valence electrons, which are still held by the carbon atoms, and which give the reducing power to the leuco-dye. We could use the Lewis-Langmuir style of writing such a pair, as $\odot$, but this does not seem to me to bring out quite so clearly the negative character of the charges in contrast to the positive charge on the oxidizing atoms. It is evident that, in the indophenol dye itself, there is still such a pair of electrons in the hydroquinoid nucleus on the right.

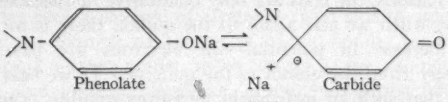
It will be seen that by oxidizing the leuco-dye, we have invested the oxidized carbon atom $\overset{+}{\underset{+}{C}}$ with oxidizing power, that is, with the tendency to recapture its two lost electrons. This oxidizing quality is a very powerful one, for it is important to recall that the quinones—and this is a quinone derivative—belong

to the most powerful organic oxidizing agents we have. With the exception of some nitro-derivatives, they are the only organic oxidizing agents that are widely used. This powerful oxidizing atom $\overset{+}{\underset{+}{C}}$ has the reducing carbon atom $\overset{+}{\underset{+}{C}}$ *in close proximity.* It attracts the pair of electrons represented by ⊖, loosens them from the ordinary intra-atomic restraints by bringing them to the outer valence shells, and thereby makes it possible for them to vibrate under the impact of the waves of white light. These are the electrons then that give the red color to indophenol. In every organic dye[7] we have a strong oxidizing component close to a powerful reducing component. The attraction of the oxidizing component, usually $\overset{+}{\underset{+}{C}}$, for the electrons of the reducing component, usually $\overset{+}{\underset{+}{C}}$, gives us that element of a pair of electrons ⊖ or ⊙ held in the proper restraints between the attraction of the positive nucleus of their own carbon atom and the attraction of the outside oxidizing positive carbon atom, which makes the vibration of the pair of electrons and the absorption of definite groups of wave-lengths possible. The complementary color is produced thus by absorption, but otherwise the process is quite analogous to the production of a tone from a violin string, firmly stretched between the bridge and the neck of the violin, under the impact of the bow.

It is clear that the *oxidizing half of the dye* is the *chromophoric group* of the older structural theory; the *reducing half* contains the *auxochromic group,* the introduction of which into the dye molecule is now indeed recognized as necessary to lend strong reducing power to half of the dye molecule. Thus, aniline $H_2NC_6H_5$ has only the faintest reducing power, and phenyl-imido-quinone (II) is only yellow (owing to the action of the oxidizing quinone group on electrons in the quinone group itself). But para-oxy-aniline $H_2NC_6H_4OH$ (para-aminophenol) is a very powerful reducing agent, and with the conversion of the aniline group in II by the introduction of the auxochromic group OH into a strong reducing group, we get the real indophenol dye I, a red dye.

We have now to determine the function of the third fundamental factor of the structural theory, salt formation, which very commonly develops the deepest and most intense colors in dyes. Our photographic developers, quinol and para-aminophenol, are in themselves hardly strong enough reducing agents to develop

plates and films; we invariably add *alkali* to them. The addition of alkali tremendously increases the reducing power of these agents—that is, their salts are far more powerful reducing agents than they are themselves. Or, in other words, in such salts, the pair of reducing electrons are far looser than in the phenols, and freer to escape. We shall demonstrate these relations presently. For the moment, it is quite clear, from the point of view of this theory, that the addition of alkali to indophenol deepens its color from red to indigo blue and intensifies its color so that the solution is opaque, because it brings out the full reducing power of the quinol group, and loosens the pair of electrons so that they vibrate more freely and absorb longer and more light waves. The explanation of this effect of alkalies is probably to be found in the fact that they form highly ionized salts, and the electrons are much freer in ions than in non-ionized molecules. The highly ionized $Na_2^+ S^=$ is a far more powerful reducing agent than the scarcely ionized H_2S, because the reducing power resides in the ion $S^=$. It is to be suspected that tautomeric salts, alkali carbides, are formed



(VIII)

and that the carbide ions represent the real reducing groups in the dyes, the photographic developers, etc. We recall that a carbide like zinc methyl catches fire spontaneously in the air.

Let us try to demonstrate some of these relations experimentally. We have here some quinol. It is quite colorless. It has reducing power, but no strong oxidizing component in the molecule. We have here some of its oxidization product, benzoquinone of a bright yellow. Benzoquinone is one of the most powerful oxidizing agents known among organic compounds, capable of oxidizing sulphur dioxide to sulphuric acid. It owes its own yellow color to the effect of its powerful oxidizing atom (presumably $^{+}_{+}C^{+}_{+}$) on electrons of a neighboring carbon atom.

Now, if we mix quinone and quinol in molecular proportions, they combine and form quinhydrone, and we have in the same molecule, a powerful oxidizing and a strong reducing component. We note the color deepening; in solution a brown-red is produced.

But quinol needs alkali to develop its strongest reducing power—and when we add alkali to the quinhydrone solution, the result is as anticipated, but startling in its intensity; a deep, almost black, color is produced and the solution is opaque.

Further, oxidation-reduction reactions lend themselves to measurements of the intensity of their forces with the aid of a voltmeter. We have here a rough potentiometer or chemometer of a type first recommended by Ostwald, and we observe there is only a very slight potential difference if we place quinone in one cell, quinol in a second cell, both containing sodium chloride solution and connected on the one hand by a U-tube containing the same solution, and on the other, through platinum electrodes with the chemometer. The exact potential, according to well-established laws governing reversible oxidation and reduction reactions of this type, depends on the relative concentrations not only of quinol and quinone in their respective beakers, but also on the concentration of quinone in the quinol solution and of quinol in the quinone solution. These are not controlled here, beyond the fact that very pure products were used, but for this and other obvious reasons, the tests are only qualitative in character.

Now, when we add alkali to the quinol, there is an extraordinary increase in potential—the electrons are passing now very freely from the quinol to the quinone. If we bear in mind the fact that such an instrument measures roughly *exponents* of concentrations or activities, we can appreciate the very great significance of the result.

It is a matter of further interest that when salt formation of basic dyes occurs with acids, with the production of maximum depth and intensity, the acid is found in the *oxidizing* component of the dye molecule. Thus, pararosaniline $NH:C_6H_4:C(C_6H_4\text{-}NH_2)_2$ (IX) is yellow, but its hydrochloride $ClH_2N:C_6H_4:\text{-}C(C_6H_4NH_2)_2$ (X) is the brilliant and intense red dye, magenta. It is significant that acid intensifies the *oxidizing* power of a quinoid just as alkali intensifies the reducing power of a quinol group. Thus, if we add an acid to quinone in our little experiment, we observe that we obtain a still higher potential, the maximum obtainable from this system. The deepening of color, then, resulting from salt formation with acids in the quinoid or chromophoric group, is associated with an increase in the oxidizing power of the group, which means an increase in its power to

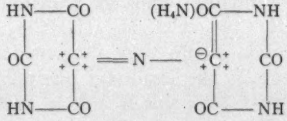
attract and loosen the electrons of the reducing group. Hence they are capable of longer vibrations, of absorbing light waves of greater length, thereby producing the *deeper* complementary colors, and hence they are capable also of absorbing such light waves more completely, thereby developing *more intensely colored* dyes.

On the other hand, an acid combined with the reducing auxochromic groups, destroys their reducing power and affects the color of dyes accordingly.‡ Thus the trihydrochloride of pararosaniline $HClH_2N : C_6H_4 : C(C_6H_4NH_2HCl)_2$ is yellow, exactly as if the auxochromic groups were altogether absent.

Let us turn now to the important question of whether the electrons actually pass from side to side in such a dye molecule as expressed in equation III. Is there continuous reduction and oxidation, and is this the vibration that absorbs light and produces color? Or are the electrons merely freed from intra-atomic restraints and vibrate within the confines of the reducing atoms? The former view has been expressed, for instance, by Adams and Rosenstein [9] and H. L. Wells.[9] But against this view we have first, the objection based on theory, which we have raised before, namely, that such a passage of electrons from side to side would necessitate the changes of almost all of the bonds, for example between some sixteen atoms, in so simple a dye as indophenol (see III) and involve, therefore, atomic vibrations which we have recognized as far too slow for the speed of light waves. In the case of aceto-acetic ester, these have been demonstrated to be of quite a different order (see IV). Aside from this objection of theoretical origin, we have established in our laboratory [10] experimental facts which prove conclusively, I believe, that no actual transfer of electrons to and fro from reducing carbon to oxidizing carbon atoms underlies the absorption of light waves. The facts prove that such an absorption is caused by vibrations of electrons still held within atomic restraints of the reducing atom, but so loosened by the proximity of the oxidizing

‡ Time does not permit of the discussion of the significant changes of color of dyes like methyl violet, whose monochloride is violet and dichloride $ClN(CH_3)_2 : C_6H_4 : C(C_6H_4N(CH_3)_2)_2$ $(C_6H_4N(CH_3)_2HCl)$ green like malachite green $ClN(CH_3)_2 : C_6H_4 : C(C_6H_4N(CH_3)_2)(C_6H_5)$. The trichloride is yellow, as expected. Green is a deeper color than violet, due to the absorption of longer wave-lengths. The relations are in complete agreement with the views presented.

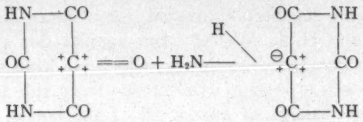
atom that the comparatively long vibrations for the absorption of components of visible light are made possible. Our experiments were carried out with derivatives of the long-known deep purple murexide, the formation of which by oxidation of uric acid is used as a test for this acid. The following diagram brings out the fact that in murexide we have the same characteristic combination of reducing ($^{+}_{+}C^{-}_{+}$) and oxidizing ($^{+}_{+}C^{+}_{+}$) carbon atoms in close proximity exactly as in the indo-dyes:



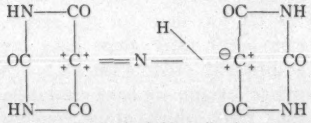
(XI)

Murexide

The dye is produced by the combination of uramil and its oxidation product, alloxan, in alkaline solution:

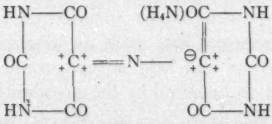


Alloxan (yellow) Uramil (colorless)



(XII)

Purpuric Acid (yellow)



Murexide (purple)

It is characteristic of murexide that acids break it up again into its components, alloxan and uramil. It is an easy matter to "tag," as it were, the reducing component and the oxidizing component. A purple murexide derivative was made by the

combining of dimethyluramil with alloxan, the group on the right in XII being made to contain two NCH_3 groups in place of two NH groups. Under the influence of acids, this dye breaks down again into the *original* components, dimethyluramil and alloxan. There has been no vibration of the reducing electrons from one group to the other. Again, another dimethylmurexide, a purple dye, was made by the combination of dimethyl alloxan with uramil. Again the dye maintained its identity, breaking down under the influence of acids into dimethyl alloxan and uramil. It is obvious that if there were oscillation from side to side, both processes would lead to a mixture of dyes from which all four components, alloxan, and dimethyl alloxan, uramil, and dimethyl uramil, would result by the action of acid. Similar experiments with "tagged" groups are being undertaken by us in the indo series of dyes.[11]

We may draw the conclusion, therefore, that color is due to absorption of visible light waves by electrons vibrating *within* the confines of a reducing atom and held loosely enough, as a result of the proximity of the oxidizing atom, for the vibrations necessary to the absorption of such long light waves.

Further conclusive support for the views expressed both in regard to a general source of color, and also to the specific question of the range of the vibrating electrons, is found, I believe, in the consideration of the fact of color from the point of view of this theory in the simpler field of inorganic compounds. My time permits only a very condensed consideration of these important compounds.

G. N. Lewis [5] has already shown that we have color development in inorganic as well as in certain organic compounds when we have an *odd* number of valence electrons (loosely held) in an atom of a compound, as in the nitrogen atom of nitrogen dioxide. Similarly, the loosely held electrons of metals are often a source of color. In a very much larger group of inorganic compounds, color is produced, I believe, by the proximity of a strong reducing atom to a strong oxidizing atom, exactly as in the case of the dyes we have discussed.

A few well-known cases, first, of color production by the combination of oxidized and reduced atoms of the same element will illustrate the general principle. For instance, here we have a series of changes of color, which closely parallel the quinol-

quinone experiments we have made. Ferrous hydroxide, when quite pure, is colorless like quinol; ferric hydroxide and ferric oxide are red, a result of the effect of the oxidized ferric atoms on the electrons of the oxide atoms $(Fe^{+++})_2O_3^{=}$, as we shall see presently. Now, if we precipitate ferro-ferric oxide from a mixture of ferrous and ferric salts, we obtain the maximum intensity of color, the jet black of magnetic iron ore. This color is due to the vibration of the valence electrons remaining in the ferrous atoms—*tending* to go over into the ferric atoms, but not quite doing so! That there is such a tendency is illustrated by the potential which we obtained when we oppose an ordinarily pure ferrous salt against an ordinarily pure ferric salt in an electric cell. We do not need salt formation to bring out the maximum color in ferro-ferric oxide, as we did with quinhydrone, because the valence electrons in atoms of the metallic elements like iron, as is well known, are much more loosely held than they are in carbon. Besides, ferro-ferric oxide is a salt, a ferrous ferrite.

In the deep blue iron dyes, prussian blue and Turnbull's blue, we again have the significant combination of the reducing ferro-atoms with the oxidizing ferric atoms. It is a common enough relation in inorganic compounds (minium, plumbous plumbate, is another well-known instance).

These illustrations do not shed any light on the question of whether the color is due to vibrations of electrons within the confines of reducing atoms or to an oscillation to and fro from atom to atom. But our next illustrations give a very positive answer to this question, for color is produced even more commonly by heterogeneous combinations of reducing with oxidizing atoms. The series $Zn^{++}O^{=}$, $Cd^{++}O^{=}$, $Hg^{++}O^{=}$ is a most significant one. As the color increases in depth from white to brown to brilliant red, we note the very evident fact that the *oxidizing* power of the cation, its tendency to draw electrons from nearby atoms, also increases, as the electrolytic solution tension series shows. Very obviously, the electrons vibrate within the sphere of the oxide atom $O^{=}$, say in red $Hg^{++}O^{=}$, attracted and loosened by the proximity of the positive, oxidizing mercuric atom Hg^{++}, but still not released. When the electrons do pass over to the mercury, as under the influence of heat, the compound of course breaks up and the color disappears:

$$Hg^{++}O^{=} \longrightarrow Hg^{0} + O^{0}.$$

Significant, too, is the fact that $Zn^{++}O^{=}$ with a much more stable cation Zn^{++}, when heated, turns yellow—the beginning of color!

$Zn^{++}S^{=}$, $Cd^{++}S^{=}$, $Hg^{++}S^{=}$, changing from white or faintly yellowish, to a bright yellow and then red or even black, form a similar series, $Ag^{+}Cl^{-}$, $Ag^{+}Br^{-}$, $Ag^{+}I^{-}$, another, illustrating the same principles. Permanganates $K^{+}O^{-}Mn\overset{+++}{\underset{+}{}}O_3^{=}$, and chromates $(K^{+-}O^{-})_2\,Cr\overset{+++}{\underset{+++}{}}O_2^{=}$ are other instances of intense color production due to *interatomic* oxidation-reduction potentials.

Support is also lent to the views here presented by the significant fact that all alkali and alkaline earth salts which do not contain a colored anion like chromate, are perfectly colorless. The alkali and alkaline earth cations have practically no reducing power; their halides and oxides are extraordinarily stable. Further, of all anions, the fluoride ion F^{-} is the most stable, and fluorides are all colorless unless a color-producing cation like Cr^{+++} is present. Cupric fluoride, ferric fluoride, mercuric fluoride are all colorless. At the other extreme we have *black* platinic iodide $Pt^{++++}I_4^{-}$.

All of these cases not only illustrate the application of the theory to common inorganic compounds, but also confirm the conclusion that the absorbing vibrations are *intra-atomic* and not *inter-atomic* ones.

This brings us to the consideration of a further type of color production as seen from the point of view of this theory. The intra-atomic vibrations of electrons, leading to color absorption and consequent production of the complementary color, may be due to the electrons of *partially oxidized* atoms and intra-atomic forces playing on these electrons. The chromic atom Cr^{+++} is a case in point. Its own oxidizing power is negligible; and yet Cr_2O_3 is green and anhydrous $CrCl_3$ is violet. *All* of its compounds are intensely colored, even the fluoride $Cr^{+++}F_3^{-}$. The last-named fact is convincing evidence that the source of color resides in the chromium atom Cr^{+++} itself. But in this atom *there are still three valence electrons* (indicated in the symbol $\overset{\cdot}{\underset{\cdot}{:}}Cr\overset{+}{\underset{+}{}}$). Half the atom remains reduced, half is oxidized—an intra-*atomic* picture reminding us vividly of the intra-*molecular* picture of our intensely colored organic dyes, as well as of red minium, prussian blue, black magnetic iron ore, etc.

In further support of this interpretation of the source of color of chromic salts, we find that aluminum salts, while greatly resembling chromium salts in chemical behavior, are all colorless: Al^{+++} has lost all of its valence electrons, while Cr^{+++} still has half of its valence electrons!

Certain important and interesting questions are raised by this theory, the final answer to which must be given by future investigation. It is characteristic, first, that oxidizing agents derived from highly oxidized forms of the *non-metallic* elements, chlorates, perchlorates, nitrates, are colorless, in contrast to the corresponding derivatives of metallic elements—permanganates, manganates, chromates, etc. And secondly, the compounds of the non-metallic elements in which the atoms of the latter still retain part of their valence electrons, as phosphites, sulphites, nitrites, etc., are also colorless in contrast to similar derivatives of metals such as chromic and vanadic salts. It is well known that the intra-atomic restraints on the valence electrons are weakest in the atoms of the metallic elements. It is quite possible, even probable, that on the one hand these intra-atomic restraints are too great in the case of phosphites, sulphites, etc., to permit long vibrations of the remaining valence electrons, and on the other hand, these same restraints may well lead to extreme non-polar union of the non-metallic atoms in nitrates, chlorates, etc., of the type advocated by Lewis, Langmuir, and Thomson, a union which would also interfere with longer, free vibrations of the electrons of the oxygen atoms. An investigation of the colorless compounds of these two classes for absorption in the ultra-violet promises to shed light on those relations.

But the general theory as presented does explain, I believe, from a common point of view, in a very simple and rational way, the existence of color where it actually occurs, both in the case of the brilliant dyes, and in that of inorganic pigments and many other colored inorganic compounds. The theory brings out the connection between the older structural theory of the color of dyes and the demand of the modern theory of vibrating electrons as the original source of color. The chromophore of the structural theory is the oxidizing component, and the auxochrome produces the strong reducing component demanded by the general theory as presented. The experimental evidence connecting color intensity and changes in depth of color with corresponding

changes in inter-atomic potential differences, through salt formation in the case of dyes and in many series of inorganic salts, brings, I believe, very strong support for the validity of the theory.

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[8] *Cf.* STIEGLITZ: "Qualitative Analysis," Vol. I, p. 253 (1911).
[9] ADAMS and ROSENSTEIN: *J. Amer. Chem. Soc.*, **36**, 1452 (1914). H. L. WELLS: *Am. J. Sci.*, **3**, 417 (1922).
[10] *Cf.* STIEGLITZ and SLIMMER: *Amer. Chem. J.*, **31**, 661 (1904). The work was repeated by Stieglitz and O. Eckstein and again independently by H. V. Tartar (Ph.D. Dissertation, University of Chicago, 1920).
[11] *Cf.* HELLER, G.: *Liebig's Ann.*, **392**, 16 (1912), and **418**, 259 (1919).

The Colors Due to Thin Films on Metals. C. T. HEYCOCK. (*Proc. Royal Soc.*, A 742.)—The colors referred to are such as those produced when a strip of iron is cleaned with emery and then heated at one end. It has been usual to attribute these colors to interference effects taking place between the light reflected from the two surfaces of a compound of the metal. This view has recently been subject to severe criticism by A. Mallock and by C. V. Raman, the Tamil physicist who, it will be remembered, was present at the centenary of The Franklin Institute in 1924.

"Mallock has stated that the temper colors which appear upon steel heated in air cannot represent an interference effect, because he has attempted to reduce the thickness of the film present on 'blued' steel by polishing, and has failed to obtain the yellow color which would be characteristic of a thinner film; the blue remained blue, although its intensity decreased as the film was rubbed away." The author holds, "It would surely be beyond the power of human technique to reduce a film of, say, 200 molecules thickness, uniformly to a film of 100 molecules thickness. What probably occurred was that Mallock completely rubbed away the film at some points, whilst leaving it intact at others." To test the effect of reducing the thickness of the film by another method, a series of colors was got on a strip of iron by heating it. From the cold to the hot end the order was brown, mauve, indigo, pale blue, steel color, pink-lavender, and pale steel blue. The strip was placed with the color bands vertical so

that the lower half of them was in dilute HCl. It was made the cathode and after about fifteen seconds the colors on the immersed part were found to have shifted their position. A like shift was obtained when the colors produced on silver by the gradual action of iodine vapor were made the cathode in dilute H_2SO_4. The author adduces further support for the interference theory of films from the work of C. W. Mason, who recently made the colors on steel shift position by the action of dilute HNO_3. In addition, R. C. Gale has succeeded by shifting the colors by polishing, the very method on which Mallock based his adverse conclusion. Gale has also shown that "the thickness of the film on heated iron increases as the color changes from yellow through purple to blue," by a study of the increase in weight.

Raman has held that it is not to interference but to some kind of granular structure that temper colors are due. The author's answer to this comes from a study of the colors appearing on molten lead as its temperature is raised. The film on the liquid consists of lead oxide and the author has found that colors occur no matter whether the film be solid or liquid oxide. In the liquid state it can hardly possess any granular structure. Besides this the solid film can be skimmed off and examined under the microscope where it displays no regular granular structure. The film moreover shows complementary colors by transmitted and by reflected light. This would be expected if interference causes the colors.

"Hinshelwood, who has carried out some interesting work on the production of brightly colored films on copper by alternate oxidation and reduction, states that here the colors are structural, being connected with the existence of numerous spherical granules in the film of oxide." The author is of the opinion that the phenomena of this experiment are consistent with interference being the cause of the colors. The outcome of his paper is to justify the measurements of thickness of films giving colors by the application of interference theory to the problem. G. F. S.

Bromine from Sea Water.—The modern demands for bromine in some industrial operations, such as motion picture work, general photography, medicine, and for the ethylene bromide now used in motor fuel, have led to a peculiar development in obtaining this element. The ship, *Lake Herminia*, formerly the property of the U. S. Shipping Board, has been purchased by a manufacturing corporation, renamed *Ethyl* and is to be used for extracting bromine from sea water. The ship is a 4300 tons dead-weight capacity, and has been fitted up with machinery of an improved character for the purpose of treating the sea water. As the ship will operate on the high seas, there will be no appreciable nuisance from either fumes or the discharged liquid. It is stated that 1700 gallons of sea water contain one pound of bromine. The method which has been adopted has been proved by laboratory tests to be satisfactory. H. L.

STUDIES IN PHOTOGRAPHIC SENSITIVITY.*

VI. THE FORMATION OF THE LATENT IMAGE.

BY

S. E. SHEPPARD, A. P. H. TRIVELLI and R. P. LOVELAND.

IN THE first paper of this series [1] various hypotheses on this problem were reviewed, with special reference to statistical variation of sensitivity among the silver halide grains of an emulsion. The proposed explanations were shown to fall into two groups. One of these forms the *chemical* theory. According to this, statistical variation of sensitivity is inherent, *i.e.*, exists previous to exposure to light. It is supposed to be due to "specks" or nuclei of a substance other than silver bromide, which was provisionally termed the photocatalyst. The other of these groups constitute the *physical* theory. According to it, the variation is not inherent but induced, being due to a corpuscular or discrete structure of light. It was then [2] pointed out that the phenomena of desensitizing are of great importance and might "help to judge between the two main theories."

In the second paper [3] it was shown that the action of light in bringing about developability was closely imitated by the action of hydrogen peroxide. It was pointed out that whether this agent acted indirectly by chemiluminescence, or chemically, the proportion of *active* molecules must be extremely small if any parallel to Silberstein's form of the "light quantum" hypothesis be maintained. W. Clark [4] has shown that the rendering developable of silver halide grains by sodium arsenite strikingly resembles the action of light. For a given class-size of grain the developable nuclei are scattered according to pure chance. Also, the sensitivity to arsenite is lowered by treatment with chromic acid.

In a third paper it was shown [5] the action of a desensitizer

* Communicated by Dr. C. E. K. Mees, Director of Laboratory and Associate Editor of this JOURNAL. Published as communication No. 228 from the Research Laboratory of the Eastman Kodak Company.

[1] JOUR. FRANK. INST., 194, 485 (1922).

[2] *Loc. cit.*, p. 519.

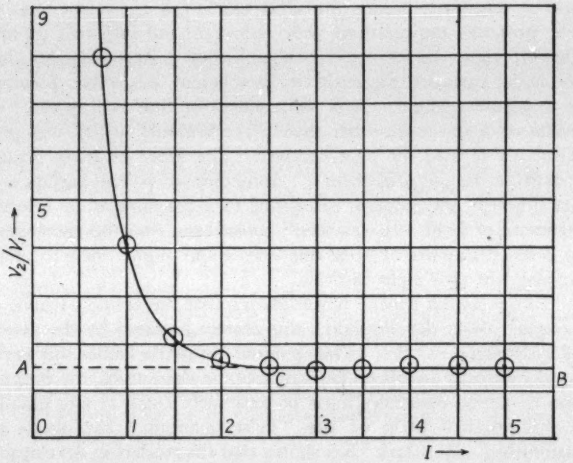
[3] JOUR. FRANK. INST., 195, 337 (1923).

[4] *Phot. Jour.*, Feb., 1924.

[5] JOUR. FRANK. INST., 196, 653 (1923).

such as chromic acid must be due to the destruction of preëxisting "specks" or nuclei, which are not silver bromide. Evidence was also given that internal "specks" exist, as well as external ones, although the latter, on the surface, are generally much the more important. Furthermore, it was shown that the "specks" on the larger grains resisted destruction by desensitizing more than those on the smaller grains. This result was confirmed by Clark [6] and will be referred to again. These results, together with those of

FIG. 1.



W. Clark and F. C. Toy,[7] leave no doubt as to the existence of a sensitivity-promoting substance other than silver bromide distributed in "specks" amongst the grains. The question now arises as to the part played by this in the formation of the latent image. The question may be divided under two heads:

(*a*) Does it lead to results incompatible with the "light quantum" theory,[8] in particular with Silberstein's application of this?

(*b*) Is the existence of such "specks" sufficient in itself to

[6] *Phot. Jour.*, Feb., 1924.

[7] *Phil. Mag.*, **44**, 352 (1922).

[8] As a theory of photographic exposure.

explain the behavior of both single-layered and multi-layer silver halide emulsions on exposure and development?

In regard to the first of these: It was shown by Jones and Schoen [9] that in the experiments of Trivelli and Righter,[10] which Silberstein used to test his equation, the number of quanta incident at $\lambda 470\mu\mu$ was about 4.7×10^{12} per cm.^{2}. This means that only a small fraction of the grain area—between one hundred-thousandth and one ten-thousandth [11]—could be regarded as sensitive, if the premise is to be maintained that a grain is made developable when hit by a single "light dart" (and absorbing one quantum $h\nu$). This view leads to a modification of the original formula. The simplest modification consists in replacing the exponent na by $n\varepsilon a$ in the formula

$$x/Y = 1 - e^{-na} \qquad (1)$$

where x/Y = proportion of grains made developable.
n = number of quanta incident per unit area.
a = projective area of grain.
and ε = fraction of the area of a silver halide grain which is "vulnerable," *i.e.*, ready to become developable (say, to lose an electron) on being hit by a "light dart." In this simple modification it is "tacitly assumed that, for equal grains at least, ε is a constant fraction."

It was considered by Silberstein [12] that the main results would not be altered much if the simple assumption is replaced by a more general one. According to this, "let the sensitive part of the area of a grain, instead of being all in a lump, consist of a number of separate vulnerable or *sensitive spots, each of area* ω, and distributed among the individual grains (each of area a) not equally but haphazardly. The necessary and sufficient condition for a grain to be made developable will now be that at least one of its spots should be hit by at least one light dart of sufficiently short wave-length." For the mathematical development for this conception, reference may be made to the original paper. It must suffice to state that if $\bar{\kappa}$ be the average number of such spots per grain, the coefficient ε, called provisionally the specific sensitivity, is now defined as

[9] *Jour. Opt. Soc. Amer.*, **7**, 213 (1923).
[10] *Phil. Mag.*, **44**, 252 (1922).
[11] L. SILBERSTEIN: *Phil. Mag.*, **45**, 1063 (1923).
[12] *Loc. cit.*

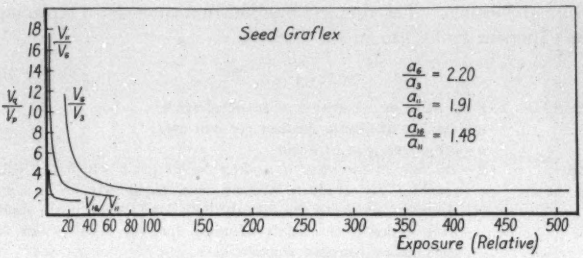
$$\varepsilon = \frac{\overline{\kappa\omega}}{a} = \frac{\overline{\kappa\omega}}{a}$$

Then if $v = ln \frac{Y}{Y-x}$ (where x/Y is the proportion of grains made developable by a given exposure), the approximate formula is derived:

$$v = \varepsilon an \left(1 - \frac{1}{2}\frac{\varepsilon an}{\kappa}\right) \qquad (2)$$

The first approximation is quite similar in form to Silberstein's original equation (1).

FIG. 2.



SVEDBERG'S DEVELOPMENT CENTRES.

In an important paper [13] The Svedberg finds that partial development, as used by Hodgson,[14] shows development to start at a number of centres. These centres he found to be distributed purely according to chance among grains of one size-class. This was shown by verifying theorem that the probability of a grain having r centres is

$$\frac{e^{-v} \cdot v}{r!} = P_r$$

From this it follows that the probability of a grain of one class-size, having one centre, is

$$P_1 = 1 - e^{-} \qquad (3)$$

where v is the number of centres formed at a given exposure. Assuming that one centre is a necessary and sufficient condition of developability, then $P_1 = x/Y$ = proportion of developable

[13] *Phot. Jour.*, **62**, 186 (1922).

[14] JOUR. FRANK. INST., **184**, 705 (1917).

grains (at given exposure). Svedberg considered that the origin of these centres—whether following previous "specks," or solely due to light—was in doubt. He concluded "that the small and the larger grains in one and the same emulsion are built up of the same kind of light-sensitive material—just as if they were fragments of different size from one homogeneous crystal."

It is obvious that this condition would practically preclude the centres from resulting from previous light-sensitive specks. For these "specks" would all have to possess the *same* light sensitivity. If now the light exposure be supposed continuous and uniform, *i.e.*, excluding a discrete structure of light, grains of the same class-size, if not all sizes, would possess the same sensitivity. For it would be sufficient for one "speck" to be present, and the exposure for all "specks" would be the same. Hence Svedberg's conclusion virtually necessitates some form of quantum theory. At the same time, it fails to give any explanation of desensitizing phenomena, which require the preëxistence of "specks" affecting sensitivity.

If Svedberg's conclusion holds, on determining the average number of centres for different grain sizes, the following relation should hold

$$v_1/a_1 = v_2/a_2 = \cdots\cdots c, \text{ a constant}$$

where v_1, v_2, etc., are the average numbers of centres per grains of surface areas a_1, a_2, etc., respectively. Hence c is the average number of centres per unit area of grain surface. Svedberg found his data [15] to corroborate this. Toy [16] has shown, however, that the evidence was inadequate. If the relationship is correct, we should also have

$$\frac{v_q}{v_p} = \frac{a_q}{a_p}$$

a constant, independent of exposure. Toy found instead that the values of this ratio fell rapidly at first with exposure, then tended to become constant and equal to the ratio of the surfaces (Fig. 1). This result was confirmed both for a high-speed emulsion with flat tablets, and a slow-process emulsion consisting of approximately spherical grains.

Toy has pointed out that his result is not only inconsistent

[15] *Phot. J., loc. cit.*

[16] *Phil. Mag.*, **45**, 715 (1923).

with Svedberg's conclusion, but equally so with the original form of Silberstein's equation

$$x/Y = 1 - e^{-na} \qquad (1)$$

For the case of two sets of grains of different sizes, $ln \frac{Y}{Y - x_1} = na_1$, and $ln \frac{Y}{Y - x_2} = na_2$.

Writing the left-hand sides v_1 and v_2, respectively, $v_1 = na_1$ and $v_2 = na_2$ or $v_2/v_1 = a_2/a_1 =$ a constant, which is the condition required by Svedberg's conclusion.

It is easily seen that this result is not changed by writing $v = n\varepsilon a$, since ε is *ex hypothesi* assumed nearly constant and independent of a or of exposure. Nor does the second approximation in Silberstein's theory appear to give a result in agreement with Toy's data.

In view of the importance of the question for the theory of sensitivity, the constancy of ε in equation (2) was put to a test, using both a high-speed (Seed Graflex) and a low-speed (Slow Process) emulsion. In the case of the former, data were available for the experiments used to test the relation of desensitizing by chromic acid to grain size.[17] For the untreated plates the results in Table I were obtained.

TABLE I.

v_q/v_p – Exposure Values. Seed Graflex.

Exposure (Relative).	1	2	4	8	16	32	64	128	256	512	a_q/a_p
v_6/v_5	....	....	....	....	11.70	4.07	2.76	2.16	2.45	2.25	2.20
v_{11}/v_6	....	17.5	6.84	3.28	3.25	2.29	1.83	...	...	...	1.91
vv_{16}/v_{11}	4.30	2.21	1.93	1.77	1.55	1.55	...	...	...	...	1.48

Plotting the values v_q/v_p as in Toy's procedure, the curves in Figs. 2 and 3 were obtained. If the limiting values of the ratios v_q/v_p are taken and compared with the ratios of grain areas, we see that the tabulated values and the curves confirm Toy's result. At low exposures the value v_q/v_p decreases rapidly, then tends to become constant and equal to the ratio of grain areas.[18]

These results were then checked, using a low-speed process

[17] JOUR. FRANK. INST., 196, 653 (1923).

[18] As pointed out by Toy, a correction for class-size width would probably improve this agreement.

emulsion, the rounded grains of which permitted greater accuracy in measuring small grains: The values for v_q/v_p for pairs of class-sizes of grain in relation to exposure are given in Table II.

TABLE II.

v_q/v_p – Exposure. Slow Process.

Exposure in Secs.	5.6	8.0	11.3	16	22.6	32	45.2	64	90.5	128	$\frac{a_n+1}{a_n}$
v_3/v_1		14.27	6.45	3.98	2.89	2.10	1.79	1.74	1.90	2.01	2.50
v_3/v_2		3.17	2.65	1.89	1.60	1.68	1.71				1 67
v_4/v_3	2.18	1.62	1.54	1.44	1.29						1.40

The results are shown graphically in Fig. 3.

RELATION OF THE SVEDBERG AND SILBERSTEIN EQUATIONS.

The condition $v_1/a_1 = v_2/a_2 = \ldots c =$ constant gives $v_1 = ca_1$, $v_2 = ca_2$, etc., so that Svedberg's equation

$$P = 100\left(1 - e^{-v}\right)$$

can be written

$$P = 100\left(1 - e^{-ca}\right)$$

where a is the area of the grain and c the average number of developable centres per unit area. This depends upon the exposure in an unknown manner. Comparing this with Silberstein's modified formula (first approximation)

$$P = 100\left(1 - e^{-n\varepsilon a}\right)$$

it appears that c should be equal to εn, that is, be directly proportional to the number of light-quanta per unit area, *i.e.*, to the exposure.

This does not agree with Svedberg's results [19] which show c increasing slowly at first with exposure, then more rapidly and approaching a linear relation. However, both the experimental results of Toy [20] and those described here indicate that c is not constant until the exposure becomes considerable, and this again is true for Silberstein's equation where n is the number of quanta

[19] Third "Hurter and Driffield Memorial Lecture," *Phot. Jour.*, July, 1922.

[20] Second paper on "Theory of the Characteristic Curve, etc.," *Phil. Mag.*, 715 (1923).

per unit area, therefore proportional to the exposure. These results raise the question of the significance of the coefficient v in the restricted equation $P = 100\,(1 - e^{-v})$. Suppose there is nothing in which the grains differ from each other previous to exposure except in size. Further let the "developable centres" be distributed among the grains[21] according to pure chance. Then it can be shown that

$$P = 100\,(1 - e^{-v}) = 100\,(1 - e^{-ca})$$

where c is a constant, by methods similar to those used by Svedberg and Toy.

Let us suppose that at any exposure there are N_1 developable centres scattered haphazard amongst grains of various sizes but total surface area A. For geometrically similar grains we may take A as the projective area. What is the probability, P_r, that a grain of surface area a will get r centres? Now $\frac{dA}{A}$ is the infinitely small probability that the surface element dA gets one centre. For a grain of surface a, $a = \int_0^a dA$, and since we may consider each dA a trial,

$$\frac{\int_0^a dA}{dA} = a/dA$$

will be the number of trials of the event. Now if p denote the very small probability that an event will happen in a single trial, the probability that it will happen r times in a very great number, N_1, trials is

$$P_r = \frac{(N_1 p)^r e^{-N_1 p}}{r!}$$

In the present case, the very small probability p is

$$p = \frac{\int_0^a dA}{\int_0^\infty dA} = a/A$$

Substituting in the above equation, we obtain

$$P_r = \frac{\left(\frac{cN_1}{A}\right)^r e^{-\frac{N_1 a}{A}}}{r!}$$

[21] Without limitation to grains of one size.

so that the probability that a grain has no centres (when $r = 0$) is given by

$$P_0 = e^{-\frac{N_1 a}{A}}$$

Hence the probability that a grain of area a will contain at least one developable centre is

$$P_1 = 1 - e^{-\frac{N_1 a}{A}}$$

or

$$P = 100\left(1 - e^{-ca}\right)$$

This is the conclusion Svedberg reached and which we have deduced more directly in the foregoing.

Now it is to be noted that while Toy [22] confirms experimentally (a) by counts of the developed centres on partially developed grains that the equation

$$P_r = \frac{v^r . e^{-v}}{r!}$$

holds for the probability that a grain of one class-size contains r centres; (b) also the consequent equation

$$\frac{x}{Y} = \frac{P}{100} = 1 - e^{-v}$$

for the proportion of developed grains, of one class-size, when v is the average number of centres per grain.

(c) He does not confirm the equation

$$\frac{x}{Y} = \frac{P}{100} = 1 - e^{-ca}$$

c = a constant, except at higher values of the exposures; our results confirm Toy's on this point.

As we have seen, the existence of desensitizing by chromic acid, etc., rules out of court any exposure theory ignoring inherent variable grain sensitivity.[23] Further, it has been shown that the assumption of specific sensitivity points differing in number from grain to grain, but not otherwise, is also incompetent.

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[22] *Phil. Mag.*, **44**, 352 (1922).

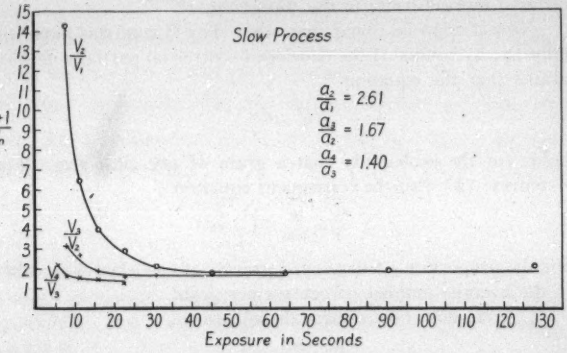
[23] Also the great differences in effective sensitivity between emulsions of identical grain-size frequency speaks against it. *Cf.* S. E. SHEPPARD, F. A. ELLIOTT and S. S. SWEET: "Notes on the Photographic Chemistry of Gelatin," *Trans. Farad. Soc.*, **19**, 262 (1923).

TOY'S THEORY OF PHOTOGRAPHIC NUCLEI.

In papers already referred to, F. C. Toy [24] has developed a theory which attempts to meet the difficulties noted. He supposes the grains contain, previous to exposure, photosensitive spots or nuclei, a more generalized equivalent of the "Reifungskeime" of Lüppo-Cramer and others.[25] These nuclei are considered not only to vary in number in different grains, but also in photosensitivity. "They are not necessarily all changed to reduction (development) centres from inactive particles by the same light energy."

It is desirable, to avoid confusion, to restrict the term "centre" to mean an actual or inferred spot ensuring developability of a grain, while "nucleus" will refer to an assumed sensitive spot prior to exposure. A centre is therefore what Toy terms an "active nucleus." The latter defines the *sensitivity* of a single nucleus as "the minimum intensity of light which must be incident upon it to make it 'active' in the presence of a developer," *i.e.*, to convert it into a centre. While this is quite understandable, it seems a pity to define sensitivity as an exposure —it should properly be the reciprocal of an exposure, or, "the

FIG. 3.



[24] *Loc. cit.*

[25] *Cf.* SHEPPARD, TRIVELLI and WIGHTMAN: JOUR. FRANK. INST., **194**, 485 (1922).

minimum intensity of light, etc.," should be termed the inertia of the nucleus, that is, the reciprocal of the sensitivity.

Proceeding from the assumption of variable sensitivity of the nuclei, thus defined, Toy assumes a certain statistical distribution of sensitivities. "Most of them will have a sensitivity near the average value for the whole, and there will be a few which are very sensitive and a few which are very insensitive. There will be none which will respond to zero intensity [26] and *none so insensitive that* it takes an infinite intensity to affect it." [27] The curve expressing the relative number of nuclei having any given sensitivity [inertia] should therefore have the general form shown in Fig. 4. This is supposed to be similar in general form to Clerk Maxwell's distribution function for molecular velocities.[28] "By similar reasoning to his, the number of nuclei (N_1) which have sensitivities [inertias] between zero and I_1 (which is the number operative when the intensity of the light is I_1) is given by the area *OAB, i.e.*,

$$N_1 = \int_O^{I_1} f(I)\, dI$$

where $f(I)$ is the distribution function. Or if N_o is the average number of nuclei [of inertias up to I_1] per grain and g the number of grains in a volume V

$$N_o = \frac{1}{g}\int_O^{I_1} f(I)\, dI = N_1/g.$$

The total number of nuclei is given by

$$N_o = \int_o^{\infty} f(I)\, dI$$

Considering now N_1 "active nuclei" distributed among Y grains of uniform size, the chance of a grain containing r nuclei is shown to be

$$P_r = \frac{(N_o)^r e^{-N_o}}{r!}$$

while the probability that a grain will have at least one is

$$P_1 = 1 - e^{-N_o}$$

[26] Spontaneously developable grains, *i.e.*, grains developing without exposure are therefore excluded.

[27] Our italics.

[28] That is, a normal or Gaussian "law of error" function.

and if x/Y is the fraction of grains made developable, $P_1 = x/Y$, and

$$x/Y = 1 - e^{-N_0}.$$

Hence, if we denote $ln \frac{Y}{Y-x}$ by S, from the above $S = N_0$. Therefore, if S is plotted against intensity, the same form of curve should be obtained as when N_0 is plotted against this variable. Now if the sensitivity [inertia]-distribution curve be of the form shown in Fig. 4 then, since

$$N_0 = \frac{1}{g} \int_0^{I_1} f(I)\, dI$$

the curve the relation between N_0 and I should be of the form shown in Fig. 5, an unsymmetrical $\int$, tending to an upper limit at fairly low values of N_0.

In the paper referred to, Toy gives data establishing a relation between S ($= N_0$ from the proportion of grain changed) and the intensity I, which is similar to that predicted for N_0 from the theory.

As will be noted shortly, the form of this curve has been questioned by Svedberg [29] as not being essentially representative of the facts. Our own data, to be noted directly, are also not in good agreement with it.

VARIATION OF GRAIN SIZE.

Curves obtained for x (number of grains changed) against $\log I$ for four different class-sizes of grains ($0.98\mu^2$, $1.75\mu^2$, $2.73\mu^2$ and $3.93\mu^2$) by Toy showed not only greater sensitivity for the large grains, but a greater slope to the curve. From these, curves relating $S(= N_0)$ to I for each grain size were plotted. These indicate a shift of the curve toward the zero of intensity as the grain size is increased. It is shown that this cannot be explained on the basis of distribution curves differing only in height of the maximum ordinate, but requires a *greater average* sensitivity of the nuclei in the large grains. That is, a bodily shift of the distribution curves nearer the zero.

We have reproduced the principal features of Toy's theory here because we consider it of great importance. As we shall show, certain of our results are not in good agreement with his

[29] SVEDBERG, SCHUNK, and ANDERSON: *Phot. Jour.*, **64**, 272 (1924).

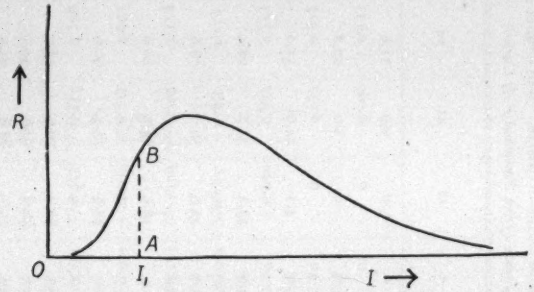
theory. Furthermore, we consider some aspects of the theory to be somewhat artificial. None the less, the idea expressed by the sensitivity distribution of the nuclei appears to us of enduring value, even should the form of it have to be considerably modified.

Criticism of Toy's theory may be divided into two parts. The first of these deals with the incomplete agreement of new experimental data with the provisions of the theory, the second with the premises themselves.

EXPERIMENTAL DEFICIENCY OF THE PHOTOSENSITIVE NUCLEUS THEORY.

The principal datum which Toy brings forward in support of his theory is the agreement of the shape of the $v(=lnY/Y-x)$:

FIG. 4.



Intensity curves as constructed from experimental data, with those predicted by the theory. As against this, Svedberg's [30] curves give a very different result. Instead of falling over to a constant value at rather low values of the number v, they are at first convex to the exposure axis and then tend to pass into a straight line. Recently Svedberg, Schunk and Anderson [31] have called attention to this discrepancy. They confirm the previously noted form of the curve (as above) for small grains, and attribute any tendency of the curve to become concave to the exposure axis to an early incidence of reversal; bathing the plates in a reversal-preventing agent tended to offset this tendency for the larger grains.

In a series of experiments made prior to this communication

[30] SVEDBERG: *Phot. Jour.*, July, 1922.
[31] *Loc. cit.*

TABLE III.

Per Cent. Developable Grains–Exposure. Seed Graflex (Untreated).

v–Exposure (from Smoothed P–E Curves).

Class-size. \ Exposure (Relative)	1	2	4	8	16	32	64	128	256	512	1024
0.115	0	0	0	0	0	0.9	11.8	31.0	42.4	56.1	68.7
	0	*0*	*0*	*0*	*0*	*0.009*	*0.155*	*0.375*	*0.551*	*0.823*	*1.163*
0.3	0	0	0	0	0	5.0	27.2	52.0	68.1	82.4	91.4
	0	*0*	*0*	*0*	*0*	*0.051*	*0.317*	*0.735*	*1.143*	*1.735*	*2.454*
0.5	0	0	0	0	4.0	22.6	51.0	74.8	85.1	92.5	97.4
	0	*0*	*0*	*0*	*0.041*	*0.257*	*0.713*	*1.378*	*1.904*	*2.597*	*3.658*
0.7	0	0	0	4.0	17.3	34.7	68.4	84.9	92.4	96.9	99.6
	0	*0*	*0*	*0.041*	*0.191*	*0.425*	*1.153*	*1.890*	*2.583*	*3.470*	*5.416*
0.9	0	0	1.3	13.0	28.0	50.6	78.6	92.0	96.0	98.7	100.0
	0	*0*	*0.014*	*0.135*	*0.329*	*0.707*	*1.514*	*2.446*	*3.219*	*4.318*	*∞*
1.1	0	0.9	5.6	21.5	38.5	64.5	86.0	94.8	99.1	99.8	
	0	*0.026*	*0.057*	*0.242*	*0.468*	*1.035*	*1.964*	*2.968*	*4.673*	*5.877*	
1.3	0	2.5	10.0	30.0	48.8	73.7	90.6	96.9	99.7	100.0	
	0	*0.009*	*0.105*	*0.357*	*0.645*	*1.338*	*2.309*	*3.466*	*5.992*	*∞*	
1.5	0	4.7	16.4	37.5	59.4	79.7	92.6	97.6	100.0		
1.7	1.0	8.6	21.9	43.3	66.6	84.8	94.3	99.0			
1.9	1.8	12.1	27.8	50.9	73.7	88.6	95.9	100.0			
2.1	3.0	16.1	32.7	55.0	78.2	91.1	97.3				

2.3	4.2	20.1	36.8	60.7	81.5	92.7	98.8
2.5	5.7	22.8	41.1	64.3	84.8	93.9	99.2
2.7	8.1	25.7	46.0	68.5	85.5	95.5	100.0
2.9	10.1	28.2	49.5	72.3	88.3	96.8	
3.1	11.9	31.9	53.8	75.6	90.7	97.5	
3.3	13.9	34.3	57.6	78.8	92.7	98.6	
3.5	15.7	37.4	61.7	81.7	94.8	99.6	
3.7	17.7	40.6	64.6	84.4	96.9	100.0	
3.9	18.8	43.7	68.8	87.5	97.5		
4.1	20.6	47.1	72.1	89.7	98.6		
4.3	22.0	49.2	76.3	91.5	100.0		
4.5	24.0	52.0	80.0	94.0			
4.7	26.2	54.8	83.4	95.3			
4.9	28.6	57.2	85.7	97.2			
5.1	31.0	58.6	89.7	100.0			
5.3	37.5	62.5	91.7				
5.5	45.0	65.0	100.0				
5.7	50.0	68.8					
5.9	61.5	77.0					
6.1	70.0	90.0					
6.3	75.0	100.0					
6.5	85.7						
6.7	92.5						
6.9	100.0						

TABLE IV.

Slow Process.

Per Cent. Developable Grains–Exposure.

v–Exposure.

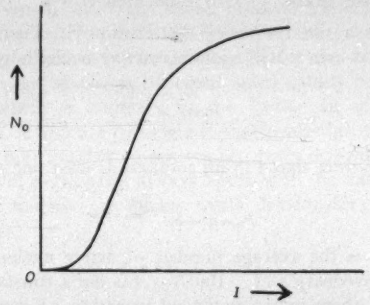
Class-size in μ^3. \ Exposure in Sec.	4	5.6	8.0	11.3	16.0	22.6	32	45.2	64	90.5	128
0.115			2.6	10.5	30.4	52.0	72.4	82.8	89.3	93.0	96.1
			0.026	*0.111*	*0.362*	*0.735*	*1.287*	*1.763*	*2.238*	*2.658*	*3.235*
0.3	13.1	19.0	30.9	51.3	76.3	88.1	93.3	95.7	98.0	99.4	99.8
	0.140	*0.210*	*0.370*	*0.719*	*1.440*	*2.13*	*2.71*	*3.16*	*3.89*	*5.05*	*6.50*
0.5	25.3	45.9	69.1	85.1	93.4	96.7	98.9	99.5	99.9	100	100
	0.292	*0.615*	*1.17*	*1.91*	*2.72*	*3.40*	*4.54*	*5.38*	*7.26*	∞	∞
0.7	52.0	73.8	85.0	94.7	98.0	98.8	100	100	100	100	100
	0.734	*1.34*	*1.90*	*2.94*	*3.91*	*4.42*	∞	∞	∞	∞	∞

of Svedberg and his associates, the following results were obtained with a relatively coarse-grained emulsion (Seed Graflex) and with a fine-grained (Process) emulsion. These results were not then checked, as now suggested by Svedberg, with anti-reversal treatment. It will be seen that the form of the curves is not at all in agreement with Toy's nor with the requirements of Toy's theory. (Figs. 6, 7, 8 and 9.)

CRITIQUE OF THE PHOTOSENSITIVE NUCLEUS THEORY.

The assumptions made by Toy appear to be somewhat arbitrary and, if not mutually exclusive, at any rate of uncertain compatibility. The *first* premise is a statistical distribution of the sensitivities of the nuclei, which is likened to the haphazard

FIG. 5.



distribution of molecular velocities in Clerk Maxwell's theory. The second premise is that the *active nuclei* (those brought to developing efficiency by a given exposure) are scattered entirely haphazard among the grains "according to the laws of chance." This is not at first (p. 354, 1st)[32] explicitly limited to grains of one class-size, but is so in the subsequent test of the assumption (pp. 357–358, 1st). Now *active nuclei* in grains of one size correspond, by definition, to all those which have required a given exposure to light to ensure developability. And since this result is supposed to be true for each exposure (when to be sure the average *number* of nuclei made active changes) each such successive group of nuclei must have been scattered entirely haphazard

[32] First paper on "Theory of the Characteristic Curve," Toy: *Loc. cit.*

among the grains of the class-size considered. By sufficient exposure, this will exhaust all nuclei occurring in this class-size. Further, this is supposed to be true for *each* class-size of grain, so that by exhaustion of all class-sizes over sufficient exposure, the dispersion of all active nuclei among the grains should be purely haphazard, according to the laws of chance. This result, without other proviso, would, as noted, lead to the conclusion of Svedberg that $v_1/a_1 = v_2/a_2 = c$, a constant, which is experimentally disproven. Actually, it appears that the condition of sensitivity variation of the original nuclei limits the haphazard distribution of the active nuclei among the *grains,* although it may remain so referring to units of area. For consider any intensity I; the N_1 *active nuclei* formed are supposedly scattered haphazard amongst all the grains (n) of total area $A = \int_0^n f(a)da$, where $f(a)$ denotes a size-frequency distribution.[33] Then the chance that a grain of area a will contain r active nuclei is given by

$$P_r = \frac{(aA_1)^r \cdot e^{-\frac{aN_1}{A}}}{r!}$$

Whence the chance that a grain contains at least one nucleus is

$$P_1 = 1 - e^{-\frac{N_1 a}{A}},$$

where N_1/A is the average number of active nuclei per unit of grain area (Svedberg's c). But N_1/A is not a constant, independent of a, if there exists statistical variation of inertias (sensitivities) of the nuclei. There appears, therefore, by this provision, some limitation on the purely chance dispersion of the active nuclei. This is still further limited by the *third assumption,* that the sensitivity of a nucleus depends upon the size of the grain in which it is present (p. 367, 1st), such "that if it is in a larger grain it is more sensitive than it would have been in a smaller one." It is assumed that this effect on the sensitivity is superposed, as an augment, on the natural or basic Maxwellian distribution of sensitivities given in the first premise. There is a certain degree of artificiality in this assumption, which is brought in *ad hoc* to explain the divergence of the v-intensity

[33] *Cf.* SHEPPARD, WIGHTMAN and TRIVELLI: JOUR. FRANK. INST., **194**, 485 (1922).

curves found by Toy from those predicted by Svedberg's theory for different sized grains.

It may be asked, if the sensitivity of a nucleus depends upon the size of grain in which it is present, upon what is the original or abstract distribution of nuclear sensitivities based? It is difficult to ascribe it any significance, as propounded, for grains of zero size, because the sensitivity is not solely a property of a nucleus. The sensitivity, or rather the inertia, is necessarily defined as a property of a grain, as the exposure required to make a grain developable. Hence there can be no actual distribution corresponding to that assumed in the first premise. On the other hand, it appears that the sensitivity of a nucleus cannot be wholly determined by the size of the grain in which it is present. For this would virtually make all grains of the same size have nuclei of the same sensitivity. And hence, however varied the *numbers* of these equi-sensitive nuclei, by definition any grain containing at least one of these would be developable for the same exposure. In that case, an emulsion of equal sized grains could give no gradation, which is contrary to the facts. In view of these uncertainties, it appears to us questionable whether the coefficient $v_{obs.}$, the average number of centres per grain determined directly, by counts, will necessarily always agree with the value calculated from the proportion of grains made developable according to the equations

$$P = 100\left(1 - e^{-v}\right)$$

or

$$v = ln\ Y/Y - x.$$

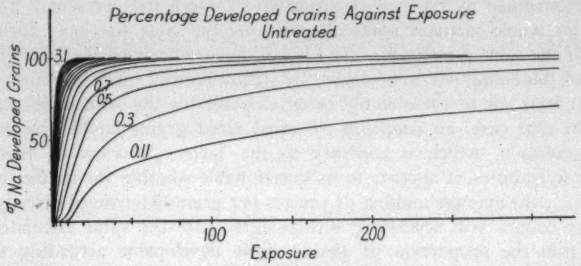
It seems possible that the former, *i.e.*, $v_{obs.}$ from actual counts, might show the ratio $v_2/a_2 = v_1/a_1 =$ constant, *i.e.*, strict proportionality between number of centres and grain area, when the values for $v_{calc.} = ln\ Y/Y - x$ show the discrepancy found by Toy and ourselves. Because in the case of *grains* made developable, the important matter is the " sensitivities " of the nuclei—whether a grain has two or three of the same sensitivity does not affect the matter. But in the case of the observed centres, it is the haphazard distribution and ensuing numbers per grain area which is revealed; but this does not determine the developability of the grains, for which the " sensitivity " (or the equivalent) of the

nuclei is responsible. While these difficulties may be overcome, they throw a certain shadow on the theoretical basis of Toy's very ingenious theory. There are, however, other and more important reasons for regarding the theory as untenable in its present form.

NUCLEI NOT PHOTOSENSITIVE.

If the preëxistent nuclei are light sensitive, and are essentially different from silver bromide, their spectral absorption should determine the spectral sensitivity of the material, or at any rate powerfully affect it. We have recently determined the spectral sensitivity of certain plates before and after desensitizing with

FIG. 6.



chromic acid according to methods which we have already described.[34] We find the same relative spectral sensitivity, in the blue-violet region, after desensitizing, as before, this distribution corresponding to the absorption spectrum, approximately, of gelatino-silver bromide. This work is being repeated, with greater spectral dispersion; the experiments at present are insufficient to permit definite statement that there is *no* shift of relative spectral sensitivity. They do show definitely that if any it is very slight, and in no way comparable with the great fall in absolute sensitivity. This conclusion is moreover confirmed by Toy's result[35] that on exposing to a mercury arc lamp at Å.U. 4358, 4062 and 3650 "the experimental relation between the quality of the incident light energy and the number of centres produced is just what is to be expected when allowance is made for the

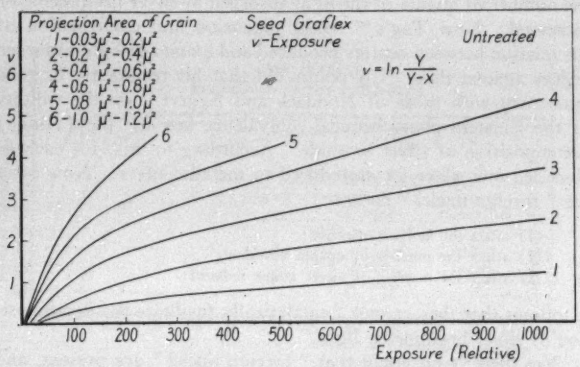
[34] JOUR. FRANK. INST., 196, 653 (1923).

[35] T. C. TOY: *Trans. Farad. Soc.*, 19, No. 56, Pt. 2, p. 294 (1923).

light absorption by the silver bromide grains"—the agreement being improved when the light absorbed is reckoned in quanta.

From this Toy himself draws the tentative conclusion that the actual substance which is changed by light in the formation of the latent image is silver bromide—"the function of the traces of foreign matter at the centre [nuclei] is to facilitate, catalytically, the decomposition by light." It is evident that even this conclusion, *viz.*, that the nuclei are not themselves photosensitive,

FIG. 7.



but catalyze the decomposition of silver bromide by light, would require considerable modification of Toy's theory of "sensitive nuclei" of varying sensitivity. But, the question arises, how are we to conceive the "catalytic facilitation of the decomposition of silver bromide by light" if there is no spectral or optical sensitizing? Evidently this conclusion, if rigorously confirmed, disposes of several suggestions as to the nature of the foreign material and its sensitizing action. First, a photo-electric effect on colloid silver, either in the form suggested by Renwick [36] or in that by Sheppard and Wightman,[37] seems excluded. This is equally the case for the suggestion of Clark [38] that "the material other than silver bromide" operates on the lines of the adsorbed

[36] *J. Soc. Chem. Ind.*, **39**, 156 (1920).
[37] *Science*, **58**, 89 (1923).
[38] *Brit. Jour. Phot.*, Dec. 14, 1923.

hydroxyl ions in Fajans' and Frankenburger's experiments[39]—the hydroxyl ion giving off more readily "electrons to the silver ions, that is, at a smaller value of $h\nu$, than the bromide ions." It is precisely *not possible,* according to the foregoing conclusions, for the foreign material to do this. What other "catalytic facilitation of the decomposition of silver bromide by light" is possible? Obviously it might next be assumed that the *number* of silver atoms affected, *i.e.,* reduced to metallic silver by light, is increased at the same wave-length. But this could only occur by the number of quanta of the light absorbed by silver bromide being increased. Now Toy's[40] recent extension and confirmation of the relation between centres produced and *quanta* of light absorbed argues against this. Toy points out that his results are in good agreement with those of Noddack and Eggert[41] on the validity of the Einstein photochemical equivalence law for the (visible) decomposition of silver bromide. According to this, for each $h\nu$ absorbed one silver ion is reduced to metallic silver. Now since the "foreign nuclei" do not:

(I) affect the $h\nu$ limit effective;
(II) affect the number of quanta absorbed;
(III) affect the number of silver atoms reduced;

it follows that they cannot "catalytically facilitate the decomposition of silver bromide by light."

Yet there is no doubt that "foreign nuclei" are present, and that their presence brings about developability of the grains at much lower intensities of light than in their absence. How is this to be explained?

CONCENTRATION SPECK THEORY.

The following theory of the nature of the nuclei has been arrived at largely by a process of elimination. It may be overturned, or modified, by future work, but we believe it to explain practically all the known facts. It is evident, from what has just been said, that the only thing left which the nuclei *can do* is to *concentrate* the silver atoms reduced by the light absorbed by silver bromide. We suggest that this is the necessary and suffi-

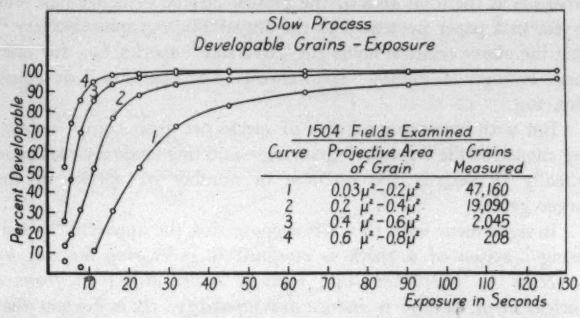
[39] *Zeitschr. f. Elektrochem.,* **28**, 499 (1922); *Zeitschr. physikal. Chem.,* **105**, 255, 273, 329 (1923).

[40] TOY and EDGERTON: *Phil. Mag.,* **48**, 947 (1924).

[41] *Zeitschr. f. Physik.,* **20**, 299 (1923).

cient condition for their action in enhancing the *developability* of the silver bromide grains at a given exposure. We suppose that there are formed on the grains, during emulsification, specks of a material, other than silver bromide, by casual adsorption and reaction with the silver bromide of a substance from the gelatine. This forms a number of "specks," scattered at random amongst the grains, and further varying in *size*. Variation and increase in size would occur from the following considerations. If we suppose the molecules of the adsorbed substance originally moving in the haphazard fashion expressed by Maxwell's law, there will be

FIG. 8.



a number of encounters with the silver bromide grains. Some of these encounters will be elastic, and some inelastic, *i.e.*, the time of relaxation of the adsorbed molecule is altered.[42] The inelastic collisions lead to a certain number of reactions with the silver halide, by which molecules[43] of the "foreign body" are fixed *in situ*. If the amount of adsorbed substance is considerably less than the silver halide in the surface layers of the grains, this process will proceed to virtual exhaustion of the adsorbed material. Further, once a speck is formed, it will tend to grow, because in its immediate neighborhood the number of inelastic collisions and fruitful encounters will be relatively greater.[44] Now it can

[42] I. LANGMUIR: *Phys. Rev.*, **8**, 149 (1916).

[43] This shall not exclude the formation of a crystalline lattice of the material formed.

[44] This may easily be observed in the deposition of noble metals by cathodic "sputtering."

be shown that on these premises, not only will the average number of "specks" on large grains tend to be greater than on small ones in the same emulsion, but also the average size of "speck" will be greater. That the average number will tend to be higher follows from the theorem that the probability of a grain of size a (surface area) fixing r specks out of a very large number possible n is given the expression

$$P_r = \frac{(na/A)^r . e^{-\frac{na}{A}}}{r!}$$

where A is the total area of the grains. Some evidence has been given, in a paper presented to the Royal Photographic Society [45] that the above relation holds for "oversize" specks, *i.e.*, for ones large enough to induce "spontaneous developability," or emulsion fog.

But with increasing number of specks per grain comes increasing chance of the "specks" growing—and this tendency may tend actually to restrict the increase in number of specks in the larger grains.

In agreement with this, we suppose that the apparent "sensitizing" action of a speck is *confined to increasing its size by accretion of photochemically reduced silver atoms to form a nucleus large enough to induce developability*. It is evident that the larger a speck is, below a certain limit giving spontaneous developability, the less the added number of silver atoms necessary to make the grain developable. Hence, the less the exposure required for this, and the greater the apparent "sensitivity" of the grain. If this is so, it would not seem necessary to assume with Toy that "the sensitivity of a nucleus depends on the size of the grain in which it is contained, and that if it is in a larger grain it is more sensitive than it would have been in a smaller one." [46] The increase in average size of specks in larger grains would tend to ensure this. However, when we consider the photochemical decomposition of the silver halide, and the process

[45] "Note on the Relationship of Photographic Emulsion Fog to Grain Size," by TRIVELLI, WIGHTMAN and SHEPPARD, communicated August, 1924, and read before the Royal Photographic Society, November, 1924. (Publ. *Phot. J.*, **45**, 134 (1925).)

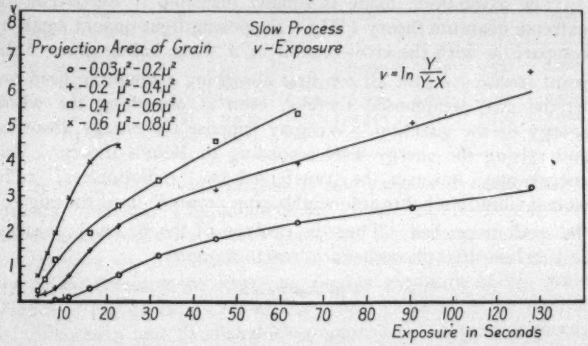
[46] F. C. TOY: *Phil. Mag.*, **44**, 367 (1922).

of concentration of the reduced silver atoms about the speck, there is a sense in which this conception of Toy's can be reinterpreted. The reinterpretation involves consequences not provided for in Toy's theory. It depends upon the premise, that the larger the silver halide grain, the larger the area illuminated, the more quanta of light are absorbed, and the greater the number of silver atoms reduced and *available for concentration.*

There are three conceptions possible of the incidence and absorption of light by the silver halide grain:

	I.	II.	III.
Incidence	Continuous	Continuous	By quanta
Absorption	Continuous	By quanta	By quanta

FIG. 9.



The first of these is in complete disagreement with the photo-active and photochemical phenomena for which Einstein's law holds. The second is the conception apparently now favored by Toy, while the third is the extreme form which Silberstein has adopted. So far as the theory of the specks is concerned, it does not appear to matter much at present whether the second or the third is adopted. In the second case, we have to suppose that all the absorbed, and thereby *quantized* energy incident on the illuminated area of a silver halide grain is used to decompose silver atoms adjacent to specks. The energy gathered over the area a is discharged quantum-wise (in formation of silver atoms) at the interface of the speck and the silver halide. The silver

halide grains are crystalline. As pointed out by J. J. Thomson,[47] "the molecules [or ions] of a solid are arranged along lattices, and if one of the molecules is struck [excited], a pulse will spread through the system, displacing the molecules as it passes over them. Thus we may regard the solid as the seat of a very large number of pulses so numerous that each molecule [or ion] is affected by a very large number of them simultaneously, and the phases of the different pulses are arbitrarily displaced." In the present case, it is the electron of the Br^- ion of the lattice which is concerned. It is reasonable to suppose that the superpositions of phase which give rise to complete displacement of the electrons will be orientated to the boundary of the speck and the silver halide, which forms a natural surface of instability.

The assumption made is equally plausible if we accept the extreme quantum theory (III). Supposing light-quanta small by comparison with the cross-section of a silver halide grain[48] the point struck, *e.g.*, the Br^- ion first absorbing a quantum need not be the one decomposed thereby, even if absorbing the whole energy of the quantum. We may suppose the energy absorbed and raising the energy level according to Bohr's theory. This energy may, however, be transferred by "radiationless" collisions [vibrations] through neighboring atoms[49] until the edge of the speck is reached. Then the electron of the Br^- ion is released and the essential photochemical reaction occurs

$$\begin{array}{ccc} Br^- & \longrightarrow & Br + \theta \\ + & & \swarrow \\ Ag + \theta & \longrightarrow & Ag \end{array}$$

That is, the released electron is accepted by a silver ion which is converted to a silver atom.[50]

This conception of the importance of the size of a grain in which a speck is present for the "sensitizing power" of the latter differs essentially from the suggestion of Toy. Furthermore, it permits the view that the probability of a developable centre forming in a grain has a certain value independent of preëxisting

[47] *Phil. Mag.*, **47**, 371 (1924). An orientating action by colloid silver nuclei on the photochemically reduced silver was suggested by Sheppard in relation to the Becquerel effect. (*Phot. Jour.*, **42**, 92 (1922).)

[48] *Cf.* L. SILBERSTEIN: *Loc. cit.*

[49] *Cf.* KLEIN and ROSSLAND: *Zeitschr. f. Physik.*, **4**, 46 (1921).

[50] S. E. SHEPPARD and A. P. H. TRIVELLI: *Phot. Jour.*, **61**, 402 (1921).

specks, and depending upon the number of light-quanta incident upon the area of a grain. The mode of introduction, in a quantitative manner, of this conception, requires further study, especially with desensitized grains. In these the influence of preëxisting specks is removed, or at least reduced to a minimum.

Referring to Table III and Fig. 7, for the untreated grains, it will be seen that there is a considerable difference not only in the absolute values, but in the shape of the curves, those for the desensitized grains being much flatter. (Fig. 10.)

TABLE V.

Seed Graflex (Treated with CrO_3).

v—Exposure. From Smoothed P—E Curves.

Class-size in μ^3. \ Exposure (Relative)	16	32	64	128	256	512	1024
0.5	0	0	0	0.069	0.220	0.547	0.865
0.7	0	0.023	0.088	0.196	0.412	0.862	1.322
0.9	0.048	0.124	0.232	0.376	0.641	1.297	1.920
1.1	0.141	0.230	0.357	0.546	0.959	1.755	2.581
1.3	0.208	0.313	0.460	0.693	1.183	2.130	3.219

It is, however, evident that if *any fortuitous collocation* of quanta [51] can start a reduction centre of perhaps only two or three silver atoms within a certain area, that this has, apart from the *competition of preëxisting specks,* the capacity of building up an actual development centre on further exposure of the grain. Hence at higher exposures an important element of the theories of Silberstein and Svedberg is recognized in the present theory. The foregoing sketch cannot be regarded as more than a very rough approximation to the interaction of specks and exposure (reckoned in quanta) in producing development centres and developable grains. According to the theory proposed, it would appear that the apparent sensitivity of silver halide grains (in the same emulsion) should increase very rapidly with the size of grain because:

(*a*) The average number of specks per grain should increase with grain size;

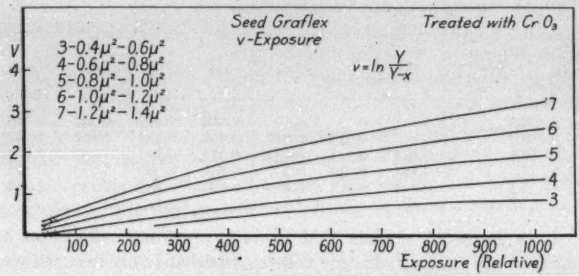
(*b*) The average size of specks should increase with grain size;

[51] Somewhat in the sense suggested by Svedberg.

(*c*) The total photochemical decomposition, *i.e.*, the available silver atoms, would be proportional to the grain area.

Now this would give an even greater increase of apparent sensitivity with grain size than is actually observed. It is, however, evident that certain restricting or limiting conditions soon come into play. While increase in the average number of specks per grain may be said to increase [52] the probability of the grain containing a speck of a certain size, *i.e.*, equivalent sensitivity, it is evident that in relation to utilization of the limited number of silver atoms available from the photochemical decomposition (*c*)

FIG. 10.



there is *competition* introduced. The chance of a given speck increasing to developable size is less the greater the number of specks present on the grain. This factor will again be modified by the distribution on the grain surface of the specks. Specks very near together might soon function as one speck. But taken by and large, it seems likely that an equilibrium will tend to be reached in these factors both with increasing exposure (number of quanta available) and, what amounts to much the same thing, with increasing grain size.

In this respect, therefore, the theory proposed reaches a conclusion similar to Toy's [53] that " when all the nuclei are operative (*i.e.*, when the exposure is large) we should expect the constant value to which the ratio $\frac{v_n + 1}{v_n}$ approaches to be the ratio

[52] As noted previously, with increasing speck growth even this may not be true.

[53] *Phil. Mag., loc. cit.*

of the surfaces of the two classes of grains." That is, we should expect to have

$$P = 100\left(1 - e^{-ca}\right) \quad c = \text{constant}$$

at greater exposures.

But, further than this, as the exposure and grain size are increased (their equivalence has already been pointed out), we should expect to find an equation of the form proposed by Silberstein, equally representative of the facts, *viz.*,

$$P = 100\left(1 - e^{-k\bar{q}a}\right)$$

where k is a constant efficiency of the specks, and $\bar{q}$ is the light energy expressed in quanta per unit area. Because as equilibrium in the competition between specks is approached, levelling up the influence of speck size, the rate of increase of developable grains will be given by

$$\frac{dx}{d\bar{q}} = k \cdot \bar{q}a\,(N_o - N)$$

whence

$$x/Y = 1 - e^{-k\bar{q}a}.$$

This condition is likely to be approached even more rapidly perhaps with *clumping* of grains, since there is a greater chance for clumps to contain one large grain. This is what Trivelli and Righter's results indicate, as well as our present results with single class-sizes of grains very little clumped. The deviation from the Silberstein equation becomes less both for increasing exposure and for increasing grain size (Fig. 11 and Table VI).

It will be understood that we do not regard Silberstein's equation as other than a limiting condition to which the behavior of a set of grains tends to approximate as exposure and grain size are increased. The original premise on which it was based, *viz.*, that it is sufficient for a grain to be struck by one quantum of light, cannot be sustained any more than the purely photoelectric theory of the latent image associated therewith. On the other hand, no definite disproof has yet been offered of the conception that the exciting light is incident in quanta as well as absorbed in quanta. Toy's criticism of this conception in regard to the wave-length factor appears somewhat beside the mark. He accepts the application of the Einstein photochemical

TABLE VI.

Slow Process.

Theoretical Developable Grains $\left(\frac{X}{\bar{Y}}\right)$ Exposure.

(*According to Silberstein Equation* $En_1 = 1.22$).

En_1–*Exposure* (*from Observed Data*).

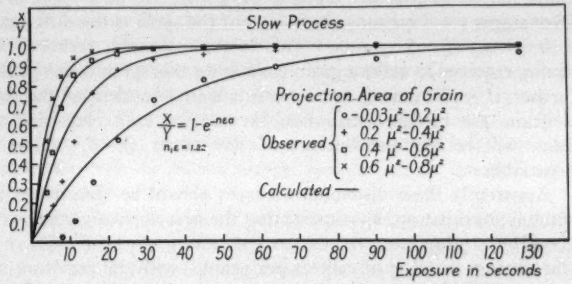
Class-size in μ^3. \ Exposure in Sec.	4	5.6	8	11.3	16	22.6	32	45.2	64	90.5	128
0.115	0.131	0.180	0.245	0.329	0.430	0.548	0.675	0.796	0.894	0.959	0.989
			0.113	*0.343*	*0.787*	*1.13*	*1.40*	*1.36*	*1.22*	*1.02*	*0.88*
0.3	0.307	0.405	0.519	0.645	0.769	0.874	0.947	0.984	0.997	1.000	1.000
	0.267	*0.495*	*0.617*	*0.848*	*1.20*	*1.25*	*1.13*	*0.93*	*0.81*	*0.74*	*0.68*
0.5	0.457	0.579	0.705	0.822	0.913	0.968	0.992	0.992	1.000	1.000	1.000
	0.146	*0.870*	*1.17*	*1.35*	*1.35*	*1.20*	*1.13*	*0.95*	*0.91*	.....	.....
0.7	0.575	0.702	0.819	0.911	0.967	0.999	1.000	1.000	1.000	1.000	1.000
	1.05	*1.35*	*1.36*	*1.48*	*1.40*	*1.12*	.....	.....	.....	.....	.....

equivalence principle to the action of light on silver bromide. But this principle has been generally supposed to carry with it precisely the relation of photochemical efficiency (like photoelectric efficiency) to wave-length which Toy repudiates.[54] The "specific photochemical effect" is, following Warburg,[55] the amount of substance transformed by 1 grain-calorie of absorbed radiation. It should be, according to Einstein's principle,

$$p = \frac{\lambda}{1.98c}$$

where $c = 14{,}300$, when λ is expressed in μ. Hence, the photochemical effect should increase linearly with the wave-length to a critical limit. This was confirmed for two spectral regions by

FIG. 11.



Warburg with HBr. But for other reactions it has not been confirmed, and the rigorous connection of the chemical change with radiation of specific frequency has been modified by Einstein in a later paper.[56] In this it is supposed that the absorption of light only leads, as an "activation," to a higher quantum condition of the molecule, the chemical reaction following an independent course.

The fact is, of course, that a rigorous quantum theory of dispersion and absorption, in particular of anomalous dispersion, selective absorption—and photochemical change—does not yet exist.

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[54] *Phil. Mag.*, **45**, 715 (1923).

[55] *Sitzungsber. preuss. Akad. Wiss.*, p. 1228 (1918); also *Z. Elektrochemie*, **26**, 54 (1920).

[56] *Physik. Zeits.*, **17**, 121 (1917).

If the theory proposed, the "sensitivity distribution," or rather inertia distribution of the nuclei in Toy's theory is replaced by a function of the size distribution of the specks. The equivalent variable in this case may perhaps be derived and specified most simply as follows: We shall suppose that the speck size can be expressed in terms of *equivalent number* of contiguous *silver atoms* in a surface layer of a silver bromide crystal. In general this will be an octahedral surface,[57] and divergences due to occurrence of cubic faces will not be discussed at this time. Now if the photochemical equivalence law holds, any number of reduced silver atoms can be regarded as equivalent to an equal number of absorbed light-quanta. Let us suppose that the *size* of a speck which makes a grain developable to be equivalent to Q silver atoms, *i.e.*, to Q quanta. Then if the actual size of a speck is S silver atoms ($=S$ quanta) the *inertia* of the speck is the difference or deficiency $Q-S$ quanta. This is the exposure, reckoned in quanta, required to make a grain containing this speck developable. Further, if we assume Q to be a constant, independent of the size of grain, the inertia-distribution curves, for each class-size of grain, will be the distributions of the values $Q-S$, where S is variable.

Apparently these distribution curves should be obtainable, to a first approximation, by constructing the first derivatives, in each class-size of grains, of the curves connecting $v=ln\ Y/(Y-x)$, "the average number of centres per grain," with the exposure or intensity of light, reckoned in quanta, in line with the method of Toy. If we set a hypothetical, but reasonable value on Q, the upper constant limit, then the values of S could be determined. More exact experiments are in progress with this object. But it may be noted that considerations of the possible early incidence of competition between specks for the available silver atoms reduced by light, as also of direct speck formation by light, make the results of this procedure uncertain. There are also the uncertainties in the precise significance of v, already noted.

There are, however, a few limiting figures worth noting in this connection. The existence of a minimum-size centre ensuring developability has been touched upon by Svedberg.[58] He

[57] *Cf.* E. P. WIGHTMAN, A. P. H. TRIVELLI, and S. E. SHEPPARD: *Trans. Farad. Soc.*, 19, 272 (1923).

[58] "Hurter and Driffield Memorial Lecture," *Phot. J.*, 62, 310 (1922).

refers to the experiments of Zsigmondy, who found the minimum size (diameter) of a gold particle capable of acting as a condensation centre to be about $2\mu\mu$. Such a particle would contain about 300 atoms of gold. Suppose a silver nucleus of the same size to be equally effective, also that we have only to consider the atoms in a surface monatomic layer.[59] Then we might assume that $Q = 200$ atoms, equivalent to 200 quanta, and this would be the minimum upper range of sensitivities of a set of grains, *viz.*, about 1 to 200. It is interesting to note that in experiments on the desensitizing of plates with chromic acid, Clark[60] finds a residual speed of about 5 H. and D. Taking 2000 H. and D. as an extreme upper limit of plate speed, this would give a range of 1 to 400. These results are obtained with very heterogeneous grain-size distributions and averages. They serve to indicate that the *order* of the size deficiencies suggested is not unreasonable. It is interesting also to note in this connection the few measurements available on the number of quanta of light incident necessary to make a grain developable. These values are very scanty, and not trustworthy save as rough averages. They have been made, in nearly all cases, with multi-layered plates, and hence even the actual energy incident on the grains is only approximately calculable.

Eggert and Noddack[61] calculated 280 quanta of light at $\lambda = 4078$ Å.U. were necessary to make developable an average grain of an Agfa special emulsion. In default of measurements, we may roughly assume $1\mu^2$ as the area of the grain. Later, Noddack, Streuber and Scheffers[62] gave 3600 quanta at $\lambda = 4360$ Å.U. as the value required to make "a grain developable."

In 1922 P. S. Helmick[63] gave some results from which he concluded that 2×10^7 incident quanta of $\lambda = 5490$ Å. were required to render a grain developable. Later[64] Helmick determined the absorptions by silver bromide—correcting for gelatine—of the wave-lengths 3650 Å.U., 3131 Å.U., 2653 Å.U. and

[59] This may be incorrect. It may be necessary to consider a layer several atoms deep, but this is less probable.

[60] *Phot. Jour.*, **64**, 91, (1924).

[61] *Sitz. Akad. Wiss. Berl.*, 1921, p. 631.

[62] *Ibid.*, 1922, p. 210.

[63] *J. O. S. A.*, **6**, 998 (1922).

[64] *J. O. S. A.*, **9**, 521 (1924).

2537 Å.U. He then counted the developed grains under a microscope, using a piece of unspecified "commercial film" as the material. No measurements of grain size were made, but an estimate of the "average grain size" from diffraction halos was .8μ diameter. Helmick gives the values in Table VII.

TABLE VII.

Wave-length Å. U.	Quanta per Grain.	Average Quanta per μ^2.	Average Quanta per μ^2 per Sec.	Average Quanta per Grain.
2537	797	179	12.4	
	780	179	27.9	770
	745	179	49.6	
2537	655	82	11.4	
	700	82	25.8	681
	562	45	12.6	562
	503	50	14	
2653	542	28	14	514
	584	72	18	
3131	402	36	18	510
	613	68	17	
3650	441	34	17	555

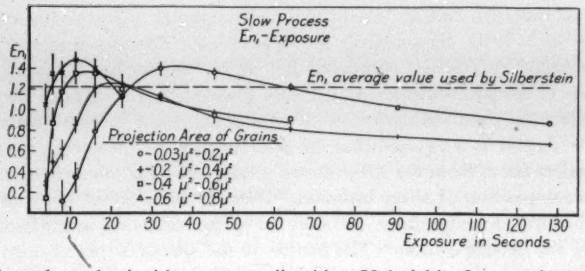
These results have no great absolute significance, owing to lack of grain measurements, absence of specification of the photographic speed, etc. Relatively it is perhaps significant that in all but one case, the quanta required per grain, at any one frequency, *increased* as the number of quanta per μ^2 (quantum concentration) increased. The order of magnitude indicated by these experiments is therefore about 500 to 800 quanta per grain of 1μ^2 for developability. But from the method of measurement, this is in any case an average of a range inside the plate, and the lower limit might be considerably less.

Jones and Schoen [65] have given some figures for the energy per cm.^{2}, also in quanta, per μ^2 at $\lambda = 4200$, to give a specified plate a density of 1.0 at $\gamma = 1.00$. They have indicated from this quanta incident on grains of various areas at their flux density. For a grain of 1μ^2 this gives about 400 quanta, for a grain of .1μ^2, about 40. There is nothing in the experiment to show, however, that grains of .1μ^2 *were* made developable by an expo-

[65] *J. O. S. A.*, 7, 213 (1923).

sure equivalent to 40 quanta per grain. Obviously the work requires extension with strictly one-grain layers of known grain sizes, and this is being done. But the quantum values found are again of about the right order of magnitude, though suggesting a speck of 500 to 1000 atoms Ag as the minimum nucleus, rather than 200. In this connection it may be noted that Helmick [66] considers that "the absolute quantity of ultra-violet energy absorbed to render a grain developable will be about 7 per cent.

FIG. 12.



less than the incident energy." Also Helmick's figures do not seem to harmonize with Toy's [67] results on the *relative* number of centres produced by light at 4058 Å.U., 4062 Å.U. and 3650 Å.U.

In computing any value of Q, the equivalent number of silver atoms for a developable centre, from a sensitivity range, this latter would have to be divided by the maximum number of centres per grain corresponding to the limiting exposure. Consequently, values estimated are likely to be upper limits.

LIMITATION OF THE ORIENTATING ACTION.

If the concentrating or orientating action of the specks is not admitted, but the other features of the present hypothesis retained, *e.g.*, absence of photosensitizing, it would be necessary to limit the growth of the specks to the required value to pure chance. This seems unlikely, in view of the large "apparent" sensitizing effects produced. On the other hand, it is probable that the concentrating

[66] *Loc. cit.*, p. 528.
[67] *Trans. Farad. Soc.*, 19, p. 290.

action is limited—as shown by the fact that with increase of exposure an ever-increasing number of "centres" appears. If the concentration effect were absolute, the number would tend to a limit earlier. Investigation of these points is proceeding.

SUMMARY.

(1) The theories of Svedberg and Silberstein on the formation of the latent image are shown to be inadequate. A criticism of Toy on these theories is experimentally confirmed.

(2) Toy's theory of photosensitive nuclei is discussed. New experimental data are found to be incompatible with the theory.

(3) It is shown that the specks of "foreign material," accepted by Toy as "photosensitive nuclei," cannot be photosensitive if the photochemical equivalence principle holds, nor can they affect the photosensitivity of silver bromide in the accepted sense.

(4) It is suggested that the sole function of the specks is to collect about them the silver atoms produced by the photochemical decomposition of silver bromide. There is no catalysis of photochemical decomposition, but only an (auto)catalyzed orientation of the decomposition. The action of the specks is purely topochemical. We suggest that they be termed "sensitizing specks."

(5) The action of light itself can supply centres in the absence of foreign nuclei. If the first reduced silver atoms have an orientating effect which autocatalytically increases with the size of the speck itself, Svedberg's conception that a certain minimum number of light-quanta must fall within a certain maximum area to form a developable centre is unnecessary.

(6) The theory suggested gives a very simple and direct explanation of the influence of grain size on apparent photosensitivity. It is shown that the theory leads over to Silberstein's as a limiting approximation when exposure and grain size are increased.

(7) The genesis and dimensions of the specks are discussed.

Metal Ammoniums.—CHARLES A. KRAUS and WARREN C. JOHNSON, of Brown University (*Jour. Am. Chem. Soc.*, 1925, xlvii, 725–731), have studied the vapor pressures of solutions of lithium in liquid ammonia. They obtained no evidence of the existence of compounds of the alkali metals with ammonia of the nature of ammonium groups. J. S. H.

OBSERVATIONS OF SPECTRO-PHOTOMETRIC MEASUREMENTS OF PAINT VEHICLES AND PIGMENTS IN THE ULTRA-VIOLET.*

BY

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In determining some properties of white pigments in the ultra-violet spectrum, Pfund [1] has demonstrated the opacity of some materials and the transparency of others. In order to extend this work to a larger number of materials, as well as to observe the behavior of the materials examined when incorporated in a paint film and exposed to light, this investigation was undertaken. The apparatus and method are those developed by Doctor Pfund at Johns Hopkins University and the work has been carried out with his coöperation and advice.

This paper will consider the following:

(1) A determination of the absorption coefficients of various paint vehicles in the ultra-violet spectrum.

(2) A determination of the reflection coefficients of various paint pigments in the ultra-violet spectrum.

(3) A determination of the effect of light on paint films made up of some of the pigments measured.

APPARATUS.

A diagram of the apparatus is shown in Fig. 1. For absorption measurements of the oils, a mercury vapor lamp is placed at L_2; a slit at S_2 has the absorption cell mounted on it; a rotating sector is used to vary the amount of light which enters the quartz spectrograph and a permanent record is made on the photographic plate. The absorption cell consists of two quartz plates separated at one end by a strip of tinfoil to form a wedge. Four positions of the wedge are used to give four different thicknesses of oil, the thickness at each position being determined by ascertaining the angle of separation of the quartz plates. This

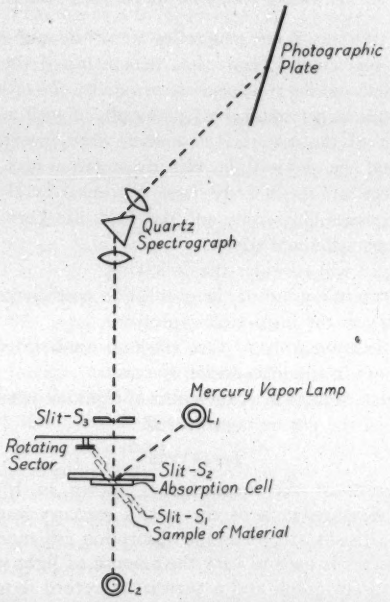
* A contribution from the Research Laboratory of the New Jersey Zinc Company. Communicated by the Chief of the Research Division.

[1] *Trans. Am. Soc. Test. Materials*, 1923.

angle was obtained by measuring the set of interference fringes produced on reflecting monochromatic light from the two surfaces of the wedge. The four thicknesses used were .0005 cm., .0014 cm., .0023 cm., and .0050 cm.

The amount of light transmitted in each case was measured by the darkening produced on a photographic negative. The density

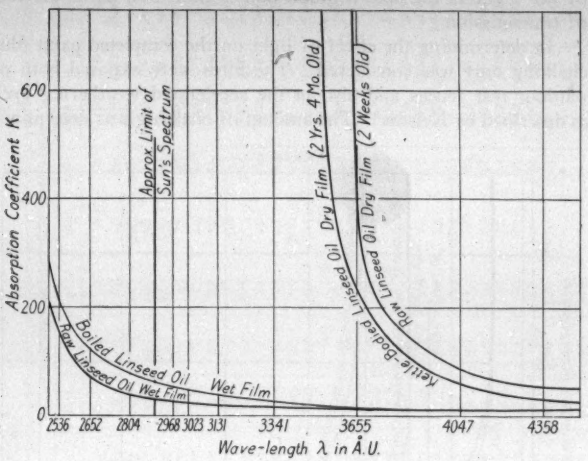
FIG. 1.



of the photographic image was determined by means of a new microphotometer designed by Doctor Pfund.

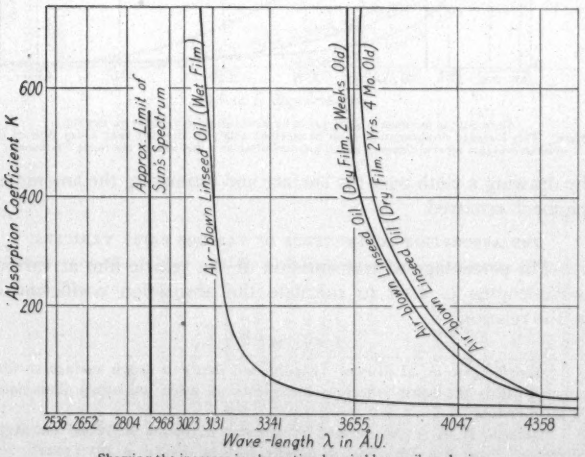
For the determination of the coefficients of diffuse reflection from dry pigment surfaces, the apparatus was patterned after that of Pfund. The mercury vapor lamp is placed at L_1, illuminating normally the sample which is placed in a cap behind the slit S_1, and the diffusely reflected light leaving the sample at an angle

CURVE 1.



Showing the increase in absorption by linseed oil on drying.

CURVE 2.

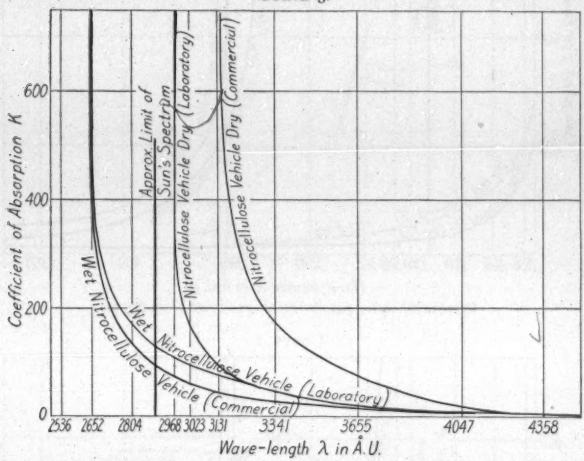

Absorption Coefficient K
600
400
200
Approx. Limit of Sun's Spectrum
Air-blown Linseed Oil (Wet Film)
Air-blown Linseed Oil (Dry Film, 2 Weeks Old)
Air-blown Linseed Oil (Dry Film, 2 Yrs. 4 Mo. Old)
2536 2652 2804 2968 3023 3131 3341 3655 4047 4358
Wave-length λ in Å.U.

Showing the increase in absorption by air-blown oil on drying.

of 50° [2] enters the spectrograph and is measured as in the case of transmission.

In determining the effect of light on the completed paint film, chalking only was considered. The films were exposed both on outdoor test fences and also in the accelerated weathering cycle as described by Nelson.[3] The amount of chalking was determined

CURVE 3.



Showing the increase in absorption by nitrocellulose vehicles on drying.
Note. This increase in absorption is to be ascribed solely to the fact that a dry film of the vehicle contains several times as much nitrocellulose as a wet film of the same thickness.

by drawing a cloth over the surface and estimating the amount of pigment removed.

THE ABSORPTION COEFFICIENTS OF VARIOUS PAINT VEHICLES.

The percentage of transmission of the vehicle film at various wave-lengths is used to calculate the absorption coefficient K in the relation

$$I = I_0 \, 10^{-kt}$$

[2] According to A. H. Taylor (unpublished data), a rough surface so illuminated yields the same reflection coefficients as when uniformly illuminated in all directions.

[3] NELSON, H. A.: "Accelerated Weathering of Paints on Wood and Metal Surfaces," *Proc. Am. Soc. Test. Materials*, Vol. 22, Part I, p. 485 (1922).

TABLE I.

Oils (Wet Film).

	Acid Number.	Absorption Coefficient K @ Wave-lengths:									
		4358	4047	3655	3341	3131	3023	2968	2804	2652	2536
Castor oil		0	0	0	2	3	2.5	2	0	0	0
Chia oil		0	0	0	0	15	25	40	95	150	800
Drier, Japan		14	25	70	160	245	375	450	800	∞	∞
Drier, cobalt		15	25	70	105	190	338	440	1000	∞	∞
Drier, lead and manganese		25	45	75	150	235	550	700	∞	∞	∞
Drier, lead and cobalt		24	25	27	32	45	75	95	165	450	∞
Linseed oil, raw		0	0	6.5	12	13	14	22	44	62	75
Linseed oil, boiled		0	0	12	25	38	50	54	85	120	225
Linseed oil, refrigerated K. V.	2.88	0	0	3	5	20	35	45	80	135	230
Linseed oil, refrigerated sup	.4	0	0	3.5	40	165	115	265	350	450	800
Linseed oil, acid refined	7.3	0	0	3.5	9	14	40	75	280	500	690
Linseed oil, raw	4.1	0	0	5.5	12.5	25	31	35	41	72	156
Linseed oil, bodied air-blown	8.9	0	2.5	6.5	28	62	800	∞	∞	∞	∞
Linseed oil, alkaline refined	2.4	0	0	6.0	25	62	81	94	142	195	245
Linseed oil, alkaline refined	.5	0	0	5	6.5	7.5	8.5	25	80	145	215
Linseed oil, acid refined	15.1	0	0	7.5	25	82	115	140	190	255	750
Linseed oil, refrigerated	1.9	0	0	5.5	16	50	72	95	135	190	250
Linseed oil, raw filtered	5.8	0	0	5.5	9	12	18	25	45	62	85
Lumbang oil		0	0	3.5	5	8.8	38	70	200	320	425
Perilla oil		0	8.8	15	45	75	100	115	168	230	340
Poppy-seed oil		0	0	2.5	4	45	85	110	215	360	460
Nitrocellulose vehicle		0	0	7.5	12	20	35	49	122	500	1000
Nitrocellulose vehicle		0	0	17	43	85	104	120	∞	∞	∞
Nitrocellulose vehicle		0	0	12	30	54	68	80	145	∞	∞
Nitrocellulose vehicle		0	0	15	35	62	80	98	150	970	1200
Soya bean oil		0	0	7.5	21	40	57	75	122	186	240
Soya bean oil, raw		0	2.2	8	24	56	80	95	152	260	370
Sunflower seed oil		0	0	2.5	5.5	68	105	140	250	640	∞
Tung oil, treated		0	2.5	16	60	140	250	315	∞	∞	∞
Tung oil, commercial China		0	6.5	21	125	550	∞	∞	∞	∞	∞
Tung oil, American		0	0	15	55	360	∞	∞	∞	∞	∞
Varnish, mixing		0	0	12	22	50	90	130	∞	∞	∞

where I is the intensity of the light transmitted through the film; I_o is the intensity of the light impinging on the film, and t is the thickness of the film in centimetres.

Curves 1, 2 and 3, and Table I present the values found for K in the case of several vehicles as well as for several dried oil films.

COEFFICIENTS OF DIFFUSE REFLECTION OF VARIOUS PAINT PIGMENTS.

Light falling upon a relatively thick layer of fine particles penetrates a large number of the particles before being completely

TABLE II.
White Pigments-Inerts.

Pigment.	Coefficient of Diffuse Reflection @ Wave-lengths:							
	5461	4358	4047	3655	3131	3024	2968	2536
Antimony oxide pigment*	97*	87	80	69	43	40	36	0
Asbestine	95	84	75	68	63	62	64	55
Barytes	93	85	75	65	66	60	60	54
Basic carbonate W. L.	95	85	83	78	69	65	62	4
China clay	93	86	76	64	62	60	59	55
Gloss white ($BaSO_4 + Al(OH)_3$)	90	83	75	72	72	71	69	60
Lithopone*	96	92	83	66	2	0	0	0
Extra-strength lithopone	96	92	83	52	2	0	0	0
Magnesium oxide*	98	98	98	98	98	98	98	98
Precipitated chalk	92	89	80	79	81	83	83	88
Silex	92.5	81	76	69.5	60	58.5	58	54.5
Sublimed white lead	96	85	82	60	58	57	56	5
Terra alba	91	90	86	86	86	85	88	90
Titanium pigment*	97	86	82	24	2	0	0	0
Whiting	93	85	77	74	65	65	60	56
Zinc oxide*	97	87	80	3	0	0	0	0
Zinc oxide (35% leaded)*	95	82	75	3	0	0	0	0
Zinc sulphide	97	86	75	37	1	0	0	0

*From data of Pfund.

reflected and returned. Therefore, any absorption shown by reflected light is essentially the absorption that would be evidenced in transmitted light. Reflection coefficients in this case are analogous to transmission factors.

A number of paint pigments, inerts, and dye toners are presented in Table II and Table III, while Curves 4 through 15 show the changes in the transparencies of several pigments when mixed with others.

EXPOSURE TESTS.

Paints were made up of a number of the pigments measured, the vehicle used consisting of linseed oil with 5 per cent. drier and 5 per cent. turpentine. Applied to wood panels, these were tested

on an outdoor exposure test fence from March 10 to October 7, 1924, a period of twenty-nine weeks. Similar panels of wood

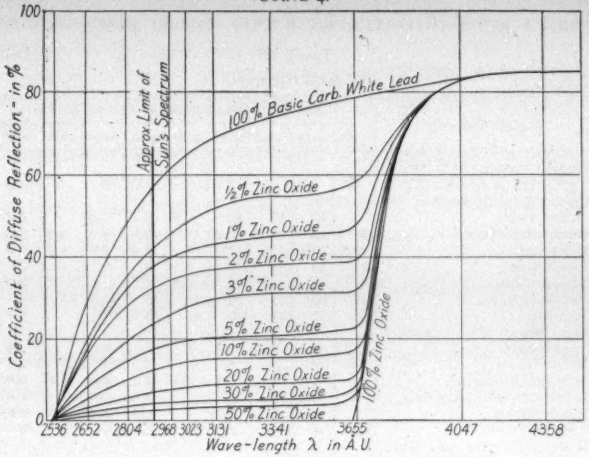
TABLE III.

Colored Pigments.

Name of Pigment.	Coefficient of Diffuse Reflection @ Wave-lengths:								
	5461	4358	4047	3655	3131	3023	2968	2652	2536
Alizarin tuscan (63% Fe_2O_3, 37% dye on $Al_2(SO_4)_3$)	8	9	8	8	5	4.5	5		1.5
Alpha naphthylamine on gloss white	7	10	15	10	9.5	8.2	6.4		4.2
Blue lead, sublimed	20	23	23.5	17.2	11.0	9.6	9.0	3.5	3.4
Blue toner	2.5	9	8	7	1	1.2	1.2	1.2	1.2
Cobalt blue	22	49	31	12	9	6	6		2
Prussian blue	1	3	3.5	4	2.5	2			2
Turquoise blue	32	50	41	35	25	25	23	22	22
Ultra blue	8	47	45	40	23	13	10		5
Bone black (71% calcium phosphate)	2	1.5	1.5	1.5	1	1	1		.5
Carbon black	5	5	5	5	5	5	5		2
Cadmium lithopone	75	6	5.5	4.4	4.4	4.4	4.3	4.2	4.0
Carmine toner on $Al(OH)_3$	6	6.5	5	5	5	2.5	1.8		1.8
Chrome green	9	5	3.8	3.7	3	2.3	2.3	2.0	2.0
Chrome yellow	60	4	4	2.5	0	0	0	0	0
Green, malachite and auramine on $Al(OH)_3$ and $BaSO_4$	12	8	7	5	4	4	4		2
Iron oxide 97%	6	5.4	5.6	5.8	6	5.3	5.7	5.9	6.3
Iron oxide 69.5%	6.8	6.7	6	6	6.5	6.5	6.8	6.9	7.0
Iron oxide 38.5%	5.5	5.0	4.6	4.7	5	5	4.9	5	5
Iron oxide 27%	6	6	5.9	5.7	6.1	6.0	6.1	6.5	7.0
Iron oxide 65%–35% $CaSO_4$	9	8	6	6	6	5	5		5.5
Lamp-black	5	4.5	3.8	4.2	4.2	4.3	4.5	4.5	4.4
Lake red	4	1.3	1	1.4	1.6	2.0	1.8		1.6
Lithol red toner $Al(OH)_3$	7	5.5	6	11.5	8.5	8		7	7.5
Lithol rubive on $Al(OH)_3$	1.5	5	6	10	10.5	10			5
Madder lake	4	6.5	9.5	11	5.3	5		1.2	1.1
Mercuric sulphide	5.5	6.3	5.7	6.0	6	5.5	5.5	5.6	5.5
Ochre, American	48	19	11	7	3.5	3	3		2
Ochre, French	50	14	10	9	8	6.5	5		5
Orange mineral	8	6.5	5.5	4.5	4.5	4.5			4.5
Para toner C. P.	5.5	5.5	5.5	5.2	5.5	3	2.2		2
Pigment scarlet toner	4	5.5	6	9	7	6.2	6		6
Pigment scarlet toner on gloss white	7	16	16.5	17	13	13		9.5	9.3
Red lead	8	6	6.3	7.2	8	7.2	7.2	7.2	7.5
Scarlet lead chromate	6.5	5	3.8	3.5	3.2	3.0	2.8	2.7	2.7
Sienna, burnt Italian	6	4	3.5	3.5	3	3	2.8		0
Sienna, American raw	21	6.5	4.5	3.5	3.2	3.2			1.0
Tuscan red	8.5	10	9.5	6	5.5	4.5	4		4
Zinc dust (blue powder)	19	20	20.5	4.2	4.5	4.5	4.3	3.8	3.75

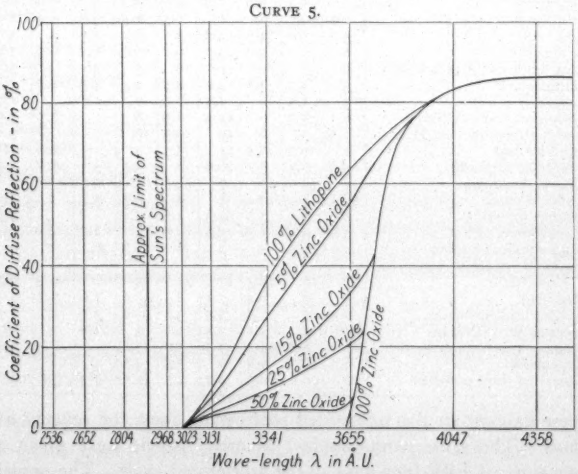
were exposed in the accelerated weathering cycle for seventy-five days. The same paints applied to metal panels were given an exposure of fifty-four days in the accelerated cycle. The percen-

CURVE 4.



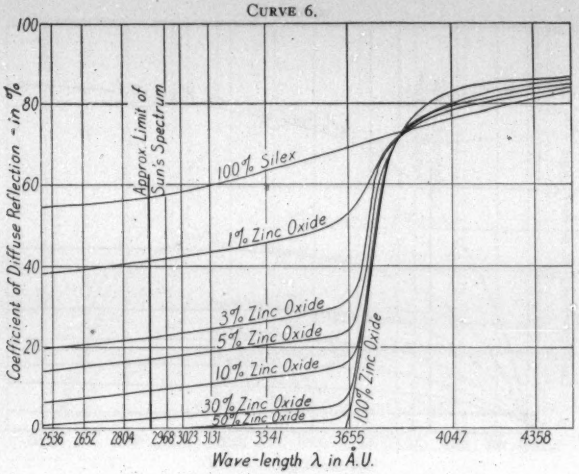
Decrease in the transparency of basic carbonate white lead when zinc oxide is added.

CURVE 5.



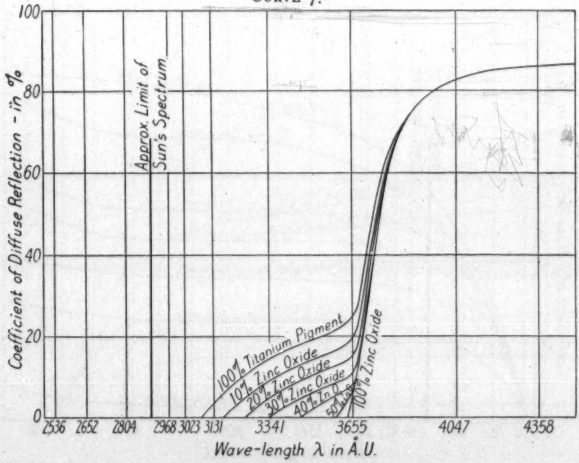
Decrease in transparency of lithopone when zinc oxide is added.

CURVE 6.



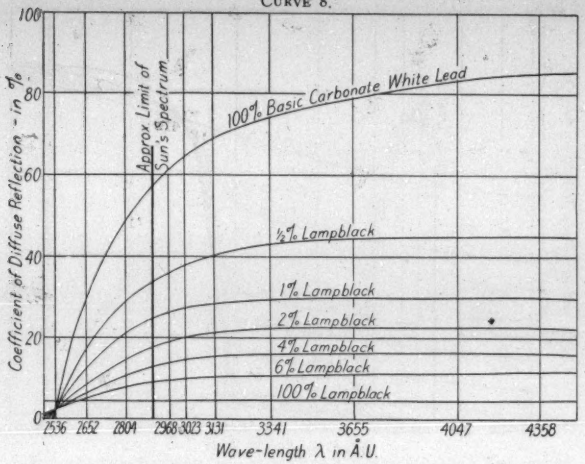
Decrease in the transparency of silex when zinc oxide is added.

CURVE 7.



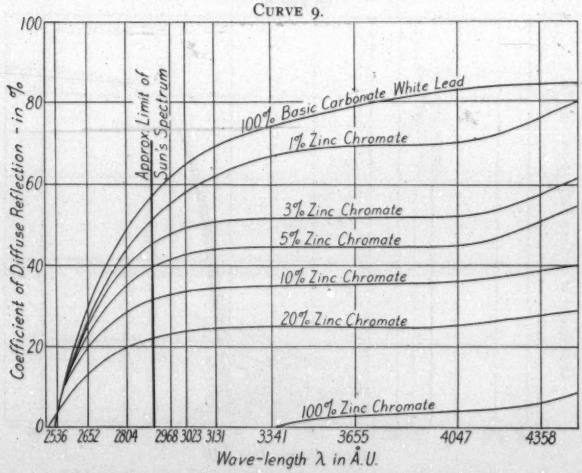
Decrease in the transparency of titanium pigment when zinc oxide is added.

CURVE 8.



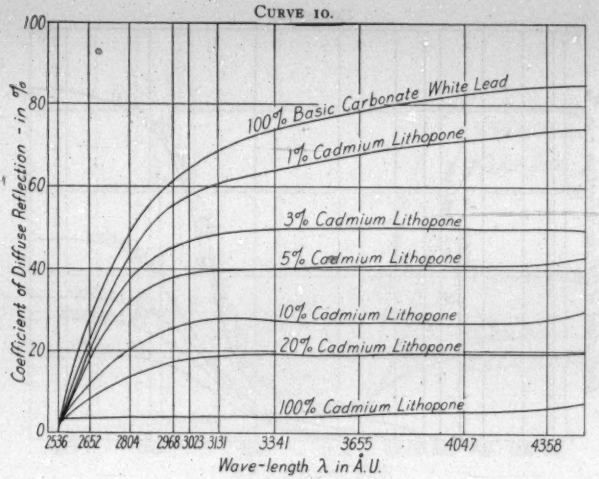
Decrease in the transparency of basic carbonate white lead when lamp-black is added.

CURVE 9.



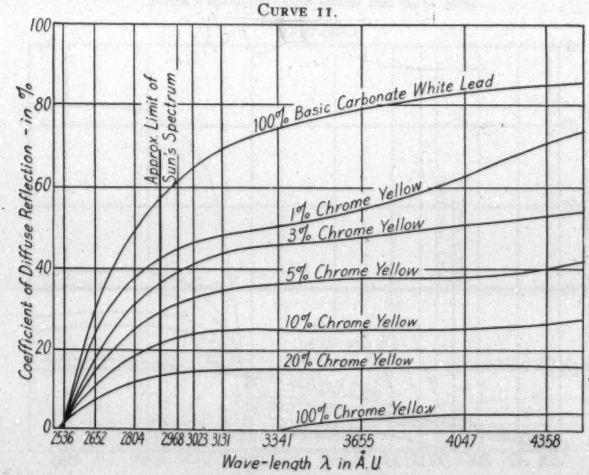
Decrease in the transparency of basic carbonate white lead when zinc chromate is added.

CURVE 10.



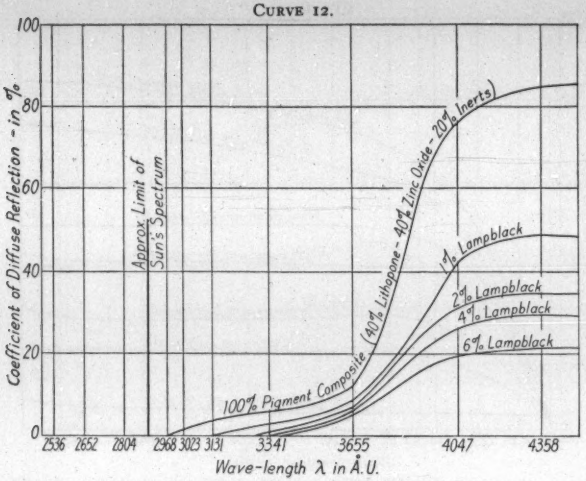
Decrease in the transparency of basic carbonate white lead when cadmium lithopone is added.

CURVE 11.



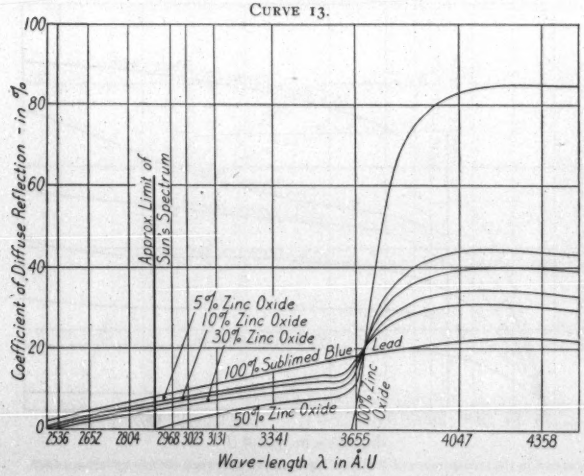
Decrease in the transparency of basic carbonate white lead when chrome yellow is added.

CURVE 12.



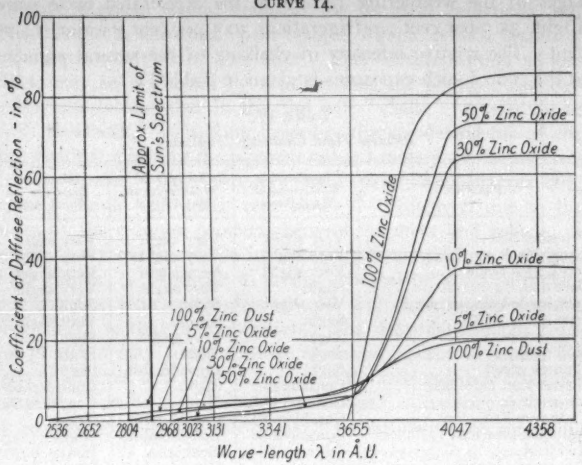
Decrease in the transparency of the pigment mixture (40 per cent. lithopone, 40 per cent. zinc oxide, 20 per cent. inerts) when lamp-black is added.

CURVE 13.



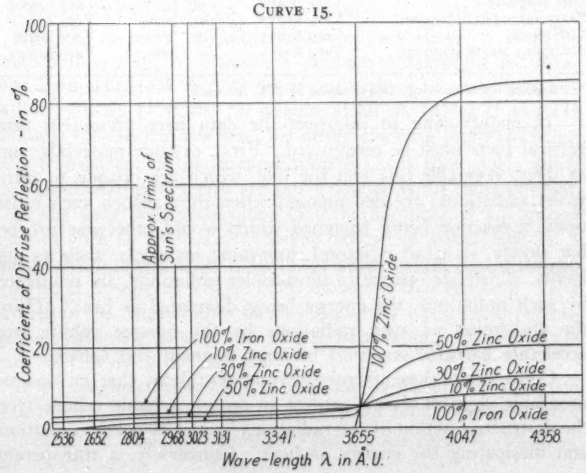
Change in the transparency of sublimed blue lead when zinc oxide is added.

CURVE 14.



Change in the transparency of zinc dust when zinc oxide is added.

CURVE 15.



Change in the transparency of iron oxide when zinc oxide is added.

tages of the weathering factors in the accelerated cycle were: Light, 55.5 per cent.; refrigeration, 30.5 per cent.; water, 14 per cent. The relative intensity of chalking of the several pigments at the end of such exposures is given in Table IV.

TABLE IV.*

Relative Final Chalking Condition.

Pigment.	Accelerated Weathering on Wood Panel.	Accelerated Weathering on Metal Panel.	Outdoor Exposure on Wood Panel.
Prussian blue	Very slight	Very slight	Very slight
Lamp-black	Very slight	Very slight	Very slight
100% zinc oxide	Very slight	Very slight	Very slight
Zinc dust	Slight	Very slight	Very slight
35% leaded zinc oxide	Very slight	Slight	Slight
Iron oxide, 97%	Slight	Slight	Very slight
Zinc chromate	Slight	Very slight	Slight
Iron oxide, 27%	Slight	Slight	Slight
Chrome green	Slight	Considerable	Slight
Scarlet lead chromate	Considerable	Slight	Considerable
Mercuric sulphide	Considerable	Slight	Considerable
Cadmium lithopone	Considerable	Considerable	Slight
Sublimed blue lead	Considerable	Considerable	Slight
Red lead	Considerable	Heavy	Heavy
Titanium pigment	Heavy	Considerable	Very heavy
Basic carbonate white lead	Heavy	Heavy	Very heavy
Basic sulphate white lead	Heavy	Very heavy	Very heavy
Zinc sulphide	Very heavy	Very heavy	Very heavy
Extra-strength lithopone	Very heavy	Very heavy	Very heavy
Lithopone	Very heavy	Very heavy	Very heavy
Antimony oxide pigment	Very heavy	Very heavy	Very heavy

*Exposure tests made and data compiled by F. C. Schmutz.

In endeavoring to interpret the data here presented, three general facts must be recognized. First, organic materials, such as dyes, vegetable oils and the like, which are opaque to ultra-violet radiations, are decomposed when they absorb such radiations, a reaction being hastened which would otherwise proceed but slowly, if at all. Second, inorganic materials, such as pigments, which are opaque to ultra-violet radiations, are unaffected by such radiations, the energy being dissipated as heat. Third, the absorption of such radiations by the opaque vehicle may accelerate harmful reactions between pigment and vehicle.

Considering these factors, Pfund postulates that an opaque, inorganic pigment should protect an opaque organic vehicle from the destructive action of the radiations by absorbing the radiations and dissipating the energy as heat. Conversely, a transparent,

inorganic pigment would transmit the harmful radiations and allow them to be absorbed by the opaque organic vehicle, resulting in the decomposition of the latter. Such decomposition of the vehicle may be evidenced by the fact that the pigment particles become unattached, that is, the film will "chalk." According to W. J. Overbeck,[4] "Chalking describes the powdering off of the paint coating, allowing the pigment only to remain on the surface, with no binder. In a properly made paint, applied correctly, chalking should take place very slowly." However, due to the nature of the reaction products between pigment and vehicle, as well as to the nature of the intermediate decomposition products of the vehicle, it is difficult to predict whether or not a paint film in which the vehicle has decomposed will chalk in an amount proportional to that decomposition. The decomposition or reaction products may form a sticky, gummy surface to which the pigment adheres, and there is consequently little apparent chalking though the film be considerably decomposed. Chalking then cannot be considered an absolute criterion of the disintegration of the vehicle film. It has been used in this investigation since it is both practical and simple. Further tests are planned in which tensile strength and elongation measurements of the film, as well as microscopic examinations, will be used.

Keeping in mind the limitations outlined above, it is to be expected then that, in general, a pigment transparent to ultra-violet light will chalk heavily while one opaque to such light will chalk very little, if at all. A consideration of Tables II and III will show that such is the case, the heavy-chalking pigments being fairly transparent in the interval 4000 Å.U. to 2900 Å.U., while the slight-chalking pigments are fairly opaque in the same interval.

It has long been recognized that the addition of an opaque pigment, such as zinc oxide, chrome yellow, or lamp-black, to a transparent pigment, such as basic carbonate white lead, titanium pigment, or lithopone, will decrease the amount of chalking. The decrease in the transparency of such pigments when small percentages of opaque pigments are added, is strikingly shown in the series of Curves 4 through 15.

It is recognized that light is only one of many factors which are involved in the deterioration of a paint film. However, the

[4] "Defects of Paint and Varnishes," *Paint, Oil and Chem. Rev.*, Aug. 13, 1924.

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result of this investigation indicates that it is an important one, since an oxidized linseed oil film absorbs completely harmful ultra-violet radiations; and we may therefore conclude that, to afford complete protection, a pigment should be opaque to ultra-violet light.

In conclusion, the author wishes to acknowledge the coöperation and advice of Mr. H. A. Nelson, Mr. F. C. Schmutz, and other members of the Research Division of the New Jersey Zinc Company, as well as the assistance of R. H. Graver and C. Hall in making the observations.

A Centrifugal Method of Making Small Pots of Electrically Fused Refractory Materials. F. S. TRITTON. (*Proc. Royal Soc.*, A 742.)—"In the course of a research on the alloys of iron and oxygen, it became necessary to hold two immiscible layers of molten iron and iron oxide at a temperature of 1540° C. It was not found possible to hold the liquid oxide at this temperature in any pot made by bonding together previously shrunk refractory material in the usual manner." Thus for the experimenter necessity became the mother of invention with the result that "a method has been developed for making well-shaped pots having a glazed internal surface of fused material not only in magnesia (M. P. 2800° C.), but also in alumina (M. P. 2050° C.), zirconia (M. P. 2700° C.) and tungsten metal (M. P. 3300° C.). The time required to produce a pot (having procured the material to be fused in the form of a powder) is about fifteen minutes, the time of actual fusion under the arc being about two minutes. For making these pots it is necessary to use refractory material which has previously been fused, so as to reduce the shrinkage to a minimum. If the material has not been completely shrunk by previous fusion, large shrinkage cavities occur in the wall of the pot."

The material after having been melted, crushed and passed through a 60-mesh sieve is put in a cup of silica mounted so that it can be electrically rotated about its axis. A thimble-shaped forming piece is pressed into the powder and removed. Graphite electrodes are inserted into the cavity thus made, the cup is made to rotate twice per second, and the arc is struck between the electrodes. The current in the arc and the speed of rotation are increased together. The refractory material begins to melt and by the centrifugal force slowly takes on a parabolic form. After sufficient material has been fused and the pot formed from it has become large enough, the current is shut off and the pot allowed to cool. In the case of alumina and zirconia which form carbides, a stream of oxygen is blown between the electrodes during the process.

G. F. S.

SOME MEASUREMENTS OF THE SPECTRAL COMPONENTS OF PLANETARY RADIATION AND PLANETARY TEMPERATURES.*†

BY

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Turning now to the ratios of the spectral components of the planetary radiation from Mars, given in Table VI, it may be noticed that the values range from 36.8 for the bright regions to 43.1, or even much higher, for the dark regions. From curve *B* (Fig. 3) the corresponding temperatures on Mars would be 5° C. for the bright regions, and 20° C. (up to 30° C. or even higher) for the dark regions. The average of all the ratios of the radiation components for the bright and the dark regions observed with the small thermocouple receiver, No. 11–21, is 41.5, the corresponding temperature being 15° C.

Using Dietzius' (*loc. cit.*) calculated temperatures of the Moon (Figs. 3 and 4, × × ×), the corresponding temperatures of the bright and the dark regions on Mars are −10° C. and 5° C., respectively; the highest values being up to 15° C. It is interesting to note that Lowell's [62] two calculations gave mean temperatures of 9° and 22° C., respectively. The average value obtained by these two methods of estimating Martian temperatures is in good agreement with the values obtained from the radiation laws.

Using lunar temperatures calculated by Doctor Menzel from the lunar water-cell transmissions and the fourth-power law gives a curve falling between *B* and *C* of Fig. 3. This gives temperatures ranging from −5° C. for the bright regions to 20° C. for the dark regions on Mars.

This method of calibration of the temperature scale is admit-

* Communicated by Doctor Coblentz and published by permission of the Director of the Bureau of Standards.

† Continued from p. 841 of the June issue.

[62] LOWELL: *Phil. Mag.* (6), **14**, p. 161, 1907.

TABLE VI.

Spectral Components in Per Cent. of the Total Radiation from Centre of Disc, also Isolated Areas, of Mars.

The Total Radiation of All Wave-lengths between 0.3 and 15μ, Transmitted by the Rock-salt Window, Is Taken 100 Per Cent.

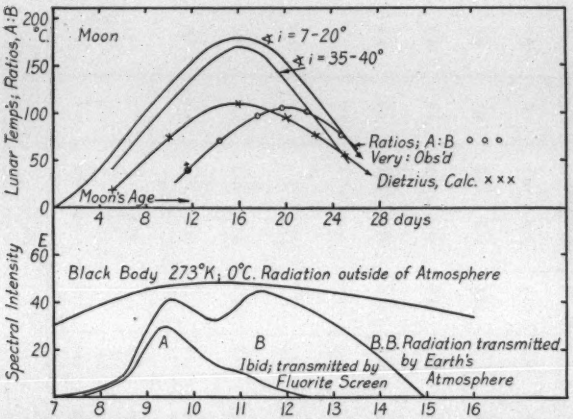
Date, 1924. M.S.T.	Thermo-couple.	Descriptive Data.	Observed Spectral Components.					Solar and Planetary.		Planetary Radiation.			Ratio A:B.	Press Aqueous Vapor.
			Fluorite λ0.3 to 12.5μ	Glass λ0.3 to 8μ	Quartz λ0.3 to 4.1μ	Solar	Water λ0.3 to 1.4μ	λ1.4 to 4.1μ	λ4.1 to 8μ	λ1.4 to 8μ	λ8 to 12.5μ	λ12.5 to 15μ		
18.4-foot Focal Length.														
											A	B	per cent.	cm.
June 24, 2:20 to 4:25 A.M.	No. 13–2	Receiver covers disc.	75.4	57.0	55.8	41.8		14.0	1.2	1.7	18.4	24.6	74.9	0.48
June 25, 3:10 to 3:40 A.M.	No. 13–2	do	77.5	53.8	....	38.8		15.0	...	....	23.7	22.5	105.5	.42
July 22, 1:45 to 3:15 A.M.	No. 13–2	do	70.4	55.1	52.3	37.4		14.9	2.8	5.6	15.3	29.6	51.7	.36
July 30, 1:35 to 3:05 A.M.	No. 12–1	Receiver covers 0.5 of disc.	73.2	57.8	54.3	37.2		17.1	3.5	8.6	15.4	26.8	57.6	.64
August 1, 2:12 to 3:12 A.M.	No. 12–1	Receiver covers 0.5 of disc, Syrtis Major.	70.5	57.5	55.0	37.0		18.0	2.5	8.6	13.0	29.5	44.1	.76
August 2, 3:03 to 3:56 A.M.	No. 12–1	do	74.4	57.1	55.0	39.0		16.0	2.1	5.6	17.3	25.6	67.7	.96
August 6, 1:12 to 1:56 A.M.	No. 12–1	do	66.3	52.3	50.5	33.5		17.0	1.8	8.0	14.0	33.7	41.7	.30
Sept. 13. 10 to 11 P.M.	No. 11–2	Receiver is 0.35 of disc, Syrtis Minor.	66.0	47.0	44.8	27.1		17.7	2.2	11.2	19.0	34.0	55.8	.58
September 14, 10:25 to 10:55 P.M.	No. 11–2	Receiver is 0.35 of disc, Mare Cimmerium.	65.7	49.8	46.3	29.3		17.0	3.5	11.1	15.9	34.3	46.4	.52

53.3-foot Focal Length.

August 14, 2:12 to 3:13 A.M.	No. 11–21	Receiver covers 0.11 of disc, Mare Sirenum.	66.0	52.0	50.0	30.8	19.2	2.0	11.2	14.0	34.0	41.3	.59
August 15, 1:15 to 1:58 A.M.	No. 11–21	Mare Sirenum; dark and light.	66.8	52.5	49.8	32.4	17.4	2.7	9.7	14.3	33.2	43.1	.54
August 18, 1:10 to 2:04 A.M.	No. 11–21	Mare Sirenum; dark.	64.7	51.1	48.6	31.1	17.5	2.5	10.0	13.6	35.3	38.6	.39
August 21, 1:27 to 2:28 A.M.	No. 11–21	do	66.5	52.9	51.0	32.5	18.5	1.9	9.9	13.6	33.5	40.7	.34
August 21, 1:27 to 2:28 A.M.	No. 11–21	Bright area north of Mare Sirenum.	66.7	53.7	....	34.9	....	...	....	13.0	33.3	39.0	.34
August 23, 1:47 to 2:17 A.M.	No. 11–21	Light region north of Mare Sirenum.	65.3	52.6	....	32.8	....	...	....	12.7	34.7	36.6	.57
August 25, 3:30 to 3:50 A.M.	No. 11–21	Light region north of beak of Mare Sirenum.	64.9	51.5	49.0	33.7	16.3	2.5	8.0	13.4	35.1	38.3	.52
August 28, 1:30 to 2:05 A.M.	No. 11–21	Solis Lacus.	67.2	50.8?	49.0	31.2	17.8	1.8	9.6	16.4	32.8	50.0	.55
September 11, 10:35 to 11:05 P.M.	No. 11–21	Syrtis Major.	67.6	52.1	....	30.8	....	...	....	15.5	32.4	47.8	.64
Sept. 13, 12:12 to 12:50 A.M.	No. 11–21	do	66.3	53.1	51.0	29.6	21.4	2.1	11.5	13.2	33.7	39.3	.44

tedly imperfect, as they all are, but this one does not involve the black-body spectral energy distribution. However, the spectral components of the planetary radiation of the Moon and of Mars were usually observed on the same night, when they were close together, with approximately the same intervening air-mass. The ratios of the planetary radiation components of the Moon and of Mars are so closely the same that it is not forcing matters to infer similar temperature conditions. The temperature of

FIG. 4.



Showing methods of obtaining temperatures on Mars by comparison of the ratio of the spectral radiation components with those observed on the Moon; also by calculation using spectral energy curves of a black body at various temperatures.

Mars is similar to that of the Moon when three to five days old. It is hoped to obtain a further calibration of the Moon's radiation and temperature, as a further check on the temperature of Mars.

In the upper part of Fig. 4, the circles (o o o) represent the observed ratios of the components of the planetary radiation from the afternoon side of the Moon, the scale of ordinates being expressed in percentages. They are interesting in showing the variation in the ratios with insolation, not taking into consideration the subsolar point. Extrapolating to the ratio 40 per cent., which is frequently observed on Mars, the corresponding temperature would be 40° C. However, by taking into consideration the angle *i*, curve *B*, of Fig. 3, is obtained.

(c) Temperature Derived from the Spectral Radiation Law.—The temperatures derived from the spectral energy distribution of a black body are minimum values. The spectral radiation of the planetary surface would no doubt be selective and its temperature would have to be higher than that of the complete radiator assumed in these calculations.

One of the difficulties involved in these calculations is the lack of exact information on transmission of the atmosphere in the

TABLE VII.

Transmission Percentages of Air Containing 1 Cm. Percipitable Water; Also Transmission Data of Fluorite Screen Used; Also the Ratio of the Calculated Spectral Components of Black-body Radiation That Would Be Transmitted by the Air and the Fluorite Screen.

Wave-length μ.	Transmission.		Black body Temp. °C.	Ratio, $\frac{\lambda 8 \text{ to } 12.5\mu}{\lambda 12.5 \text{ to } 15\mu}$ Per Cent.
	Air.	Fluorite.		
7.5	2	92	−100	23
8.0	..	90	−73	28
8.5	20	86	−23	36
9.0	..	79	0	39
9.5	87	69	27	44
10.0	..	55	100	55
10.5	67	39	127	59
11.0	..	22		
11.5	93	9		
12.0	..	3		
12.5	78	1		
13.0	..	0		
13.5	56	0		
14.0	..	0		
14.5	0	0		

spectral region extending from 8 to 15μ. The data[63] used in these calculations, including the absorption by ozone and CO_2 (also the transmission data on the fluorite screen), are given in Table VII.

The procedure followed in these calculations consisted in plotting the spectral energy curve of a black body at, say, 0° C. (see lower part of Fig. 4), which represents the spectral energy distribution outside of the atmosphere. Multiplying the ordinates of this curve by the spectral transmission of the air, a new curve is obtained, extending from 8 to 15μ, with an indentation at 10.5μ. The ordinates of this curve, which is assumed to be

[63] FOWLE: "Smithsonian Physical Tables," 7th Ed.

similar to the spectral energy distribution of the incoming planetary radiation, were then multiplied by the transmission factors of fluorite, given in Table VII, and the resultant curves were integrated. The areas under these two curves, *A* and *B*, in Fig. 4, represent the planetary radiation components extending from 8 to 12.5μ and 12.5 to 15μ, respectively. The ratio of these two areas, $A:B$, varies from 36 per cent. at −23° C. to 60 per cent. at 127° C. These calculated ratios are plotted in curve *A* of Fig. 3, which is the basis for our temperature estimates of Mars using the law of spectral radiation of a black body. This procedure is not essentially different from that of Pettit and Nicholson,[64] who attempted to fit their data to the spectral radiation curve of a black body after applying the atmospheric transmission factors.

From this curve it would appear that the calculated black-body temperatures, giving spectral components similar to those observed on Mars, range from −15° C. for the bright regions to 18° C. for the dark regions.

For the average ratio (41.5) of all the observations made with the small thermocouple receiver No. 11–21 at the 53.3-ft. focus, the corresponding black-body temperature is 10° C. as compared with 15° C. obtained by direct calibration against the Moon. As already stated, the latter value should be the higher. The temperature values which are below 0° C. are inconsistent with visual observations, showing that snow is never seen on the equator at Martian noon.[65] While this may be owing to the well-known fact that snow evaporates at temperatures below 0° C., the temperature data as a whole are consistent with other phenomena observed on Mars, showing that the temperature is above 0° C.

(*d*) *Temperatures Derived from the Total Radiation Law.*—The water-cell transmissions of the radiation from Mars, observed in 1922, were worked out by Menzel,[66] by a method suggested by Prof. H. N. Russell. This method is an improvement over the previous calculations of planetary temperatures by means of the fourth-power law of total radiation of a black body. In this

[64] PETTIT and NICHOLSON: *Publ. Astron. Soc. Pacific*, 36, p. 269, 1924.
[65] See summary discussion by PICKERING: *Pop. Astron.*, 30, p. 410, 1922.
[66] MENZEL: *Astrophys. Jour.*, 58, p. 65, 1923.

method the errors of observation are minimized because they enter the equation as the fourth root of the calculated temperature.

For the water-cell transmissions of 1922 (of which two series were available, June 15th and 18th) his calculations gave temperatures of −5° C. and −9° C., respectively. It should be noted, however, that the smallest receiver which gave a temperature of −5° C. intercepted about 0.4 of the diameter of the planetary disc, while the one having a diameter of about 0.55 of the planetary disc gave the lower value: −9° C. From the foregoing measurements, which show a steep temperature gradient from the equator to the poles and the limbs of the planet, it is evident that the highest temperature, −5° C., is an average value which should be corrected for latitude. This would raise the temperature of the equatorial region to 5° C. or perhaps even higher.

The recent measurements made by Pettit and Nicholson,[67] using a receiver which covered 0.25 of the diameter of the disc, when reduced by the fourth-power law of total radiation, indicate an equatorial temperature of +3° C. as compared with −13° C. for the whole disc.

In view of the apparent disagreement of our observed temperatures and the values previously calculated by the fourth-power law, we submitted our data to Doctor Menzel for further consideration to determine wherein, if at all, this method is at fault. For completeness of the present discussion, the following results of his calculations are included in this paper.

From the water-cell transmissions of the radiation from the whole disc of Mars, obtained on June 24th and June 25th, the calculated temperatures are 237° K. and 242° K., respectively, for the thermocouple having a rock-salt window, and 250° K. (June 25th) when the window was of fluorite. This is in good agreement with our value (water-cell transmission, 41.8 per cent.) of −20° C. taken from the calibration curve (Fig. 2) and with the measurements of Pettit and Nicholson, who obtained a temperature of 260° K. (−13° C.) for the whole disc. It represents an average temperature of about −25° C. for the whole disc, which is a different question from the one involving measurements on isolated areas.

From our water-cell transmissions of the radiation from *Syrtis Major* on September 13th, he calculated a temperature of

[67] PETTIT and NICHOLSON: *Publ. Astronom. Soc. Pacific*, 36, p. 269, 1924.

+5° C. On this night our ratio of the spectral components, $A:B$, was low, giving a temperature of −2° C., as calculated from the spectral radiation laws, and +8° C. by direct calibration against Moon. The temperatures calculated by this method range from −5° C. for the bright areas to +20° C. for the dark areas, the predominating values being +4 to +6° C. The true temperatures would be about 10° higher. Further data will be given in a separate paper on this subject.[68]

From the foregoing it is evident that these four methods are in agreement in showing that the noonday temperature of the equatorial region of Mars, at perihelion, is of the order of +10° C.

(*e*) *Temperatures Inferred from Comparisons with the Earth.*—In view of the fact that the herein-recorded temperatures seem so high, it is relevant to emphasize the fact that the irradiated dry solid surface of a planet like the Earth is at a higher temperature than the overlying atmosphere in which temperatures are ordinarily measured. The surface of loose sand and dust is at a higher temperature than that of solid rock, which affords better conduction of heat. The surface of Mars is no doubt Saharan—dry and dusty. Our observations are on the radiation emitted by the solid surface.

The Earth reflects about 45 per cent. (absorbs and scatters about 55 per cent.) of the incident solar radiation. Under these conditions the air close to the surface has a mean temperature of about 15° C., while the temperature of the dry solid surface rises to 40° C., or even higher. The intensity of the solar radiation incident upon the outer atmosphere of Mars, near perhelion, is about one-half that upon the Earth. But Mars reflects only about 15 per cent., *i.e.*, it absorbs about 80 per cent. as much of the incident solar energy as does the Earth, per unit area, with the Sun in the zenith. This would produce a temperature of 11° C. on the surface of Mars as compared with 27° C. on the Earth. The albedo of 0.15 for Mars is a mean value, and, as our measurements show, the dark regions reflect much less than the bright regions. The temperature of the solid surface should therefore be expected to rise almost as high as that of the Earth. In fact, with much clearer skies and with less air-convection, in some of the darker places on Mars the temperature should be considerably

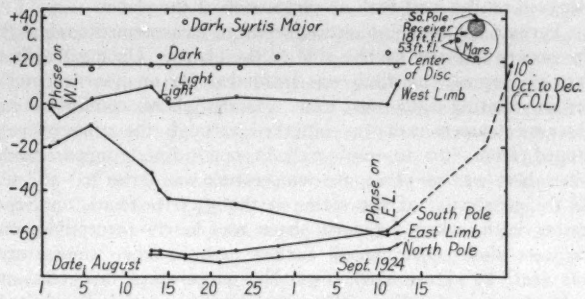
[68] MENZEL, COBLENTZ and LAMPLAND: *Amer. Astronom. Soc.*, Washington Meeting, January 1, 1925. (Abstract in *Pop. Astron.*, 1925.)

higher than observed on the surface of the Earth. Hence, with a longer summer season there should be a similar rise in temperature, especially on the south polar region of Mars.

3. SEASONAL VARIATION OF TEMPERATURES ON MARS.

The gradual change in the water-cell transmissions with change in season on Mars is evident from a casual inspection of the data assembled in Table V. It is instructive to convert these water-cell transmissions into temperatures, by means of the graph

FIG. 5.



Showing seasonal changes in temperature with advance in summer season on the southern hemisphere of Mars.

illustrated in Fig. 2. The resulting data are illustrated graphically in Fig. 5.

The measurements on the illuminated centre of the disc are interesting in showing a fairly uniform temperature of about 16° C. throughout the six weeks from August 1st to September 14th, when the series was concluded. Similarly, the temperature of the north polar region, where winter prevails, departs but little from −70° C., if we except the minimum of −75° C., observed on August 21st.

In contrast with the fairly uniform temperature conditions in the north polar region, the temperature of the south polar region, as viewed through the Martian atmosphere, as already explained, is gradually rising from −68° C., observed on August 12th, to −45° C., observed on September 12th, and +10° C. or even higher in November. This, of course, might be expected in view of the advance in the summer season on the southern hemi-

sphere, with the summer solstice occurring on October 5th. After the summer solstice there was a rapid rise in temperature (Fig. 5).

On the west limb the observed temperature was −2° to −6° C. at the beginning of August, when there was a small dark phase. When there was practically no phase on the west limb, the temperatures ranged from 0° to 4° C. At the conclusion of the series, September 12th, for reasons not yet explainable, the temperature of the whole disc seemed to be higher than usual. Hence, no emphasis need be placed upon the high value of 9° C. observed on the west limb or sunset side of the planet.

Perhaps the most interesting series of measurements relate to the eastern limb, or sunrise side of the planet. During the first part of August, this limb was irradiated for an hour or more before rotating into our view. Under those conditions its observed temperatures (as observed through the atmosphere) ranged from −10 to −20° C. At opposition, August 22nd, when there was no phase, the temperature was down to −46° C. At the conclusion of the series at the 53.3-ft. focus, on September 12th, when the dark phase was barely perceptible, on the east limb (illuminated surface, 0.976) the temperature was −60° C. How much lower the temperature falls remains to be determined. From the measurements on the illuminated north pole, where temperatures down to −75° C. were recorded, it appears that the temperature of the night side of Mars may fall below −75° C. In view of the fact that we have no way of eliminating the effect of the Martian atmosphere, especially at the south pole, where the temperature of the surface was perhaps 0° C. instead of −60° C., it is evident that the foregoing low numerical values may be subject to correction.

With the approaching culmination (October 5th) of the Martian summer, it was of interest to repeat the earlier measurements made at the 18-ft. focal length. While the measurements of September 13th were in progress, the seeing was good, giving an excellent view of the south pole, *Hellas,* and *Syrtis Minor;* also *Syrtis Major.*

All the measurements seem conclusive in showing that with the advance in the summer season on the southern hemisphere there is a gradual rise in the surface temperature of Mars. This is shown not only by the ratios of the long wave-length spectral

components, $A : B$, but also by the lower values of the transmissions through the glass screen as compared with the fairly constant values observed through the fluorite screen, which means a rise in temperature and a shift of the maximum emission towards the short wave-lengths. Under these conditions the temperature of the *Syrtis* region seems to rise to perhaps 20° C. while the brighter regions are at a temperature of only 10° C.

In concluding this discussion, it is relevant to notice (Fig. 5) that for the measurements made on different parts of the planet, on successive nights, the values seem to follow a sequence: All higher or lower than those of the preceding or following night. This does not seem to depend upon the humidity, and an explanation thereof is not at hand. It would be interesting to study this effect with variation in the solar radiation intensity which is known to fluctuate appreciably. The sudden rise in the temperature of the south polar cap of Mars after solstice is extremely interesting, indicating a rapid disappearance of the overhanging canopy (of mist, ice spicules, or whatever it may be), thus permitting the escape of planetary radiation from the surface. This observation should have an important bearing on the extent and the quality of the atmosphere of Mars. Apparently we have made a good beginning in studying the climatology of Mars.

The temperature gradient of 15° C. on the equatorial belt to −70° C. at the north pole may appear to be very large, but it is no greater than observed on this Earth.

The low temperature of the south pole, as observed with the smallest receiver, might be owing in part to the edge effect, caused by setting the receiver on the atmosphere of Mars, which, as will be noticed presently, is appreciable in extent. This would give a high water-cell transmission (Table V). On the other hand, when using a circular receiver covering 0.2 to 0.5 of the diameter of the disc, the south polar cap was only a small part of the total area intercepted (see diagram, upper right-hand corner of Fig. 5), and hence the integrated temperature is much higher, as may be noticed in the water-cell transmissions in Table V.

This study of the seasonal changes in temperature on the southern hemisphere of Mars was continued late into November, 1924, by members of the Lowell Observatory; and the results will be published in a supplementary report. The receiver then covered about 0.25 of the diameter of the disc of Mars; therefore if the

temperature had remained stationary, the water-cell transmissions should have increased to perhaps 38 per cent., as observed in July and August (Table V). However, the water-cell transmissions of the radiation from the central part of the disc continued to range about 30 per cent. showing that, if anything, the average temperature increased.

The water-cell transmissions of the radiation from the north polar region continued high, indicating temperatures of −70° C. to −80° C., as was to be expected.

The water-cell transmissions of the radiation from the south polar region are more difficult of interpretation. When the receiver covered about 0.5 the diameter of the disc (Table V) the water-cell transmissions were of the order of 39 per cent., giving an integrated temperature of −10° C., as compared with −68° C. when intercepting 0.11 the diameter. From this it would appear that, in November, when the receiver covered 0.25 the diameter of the disc, the integrated temperature should have been about −25° C. This is contrary to the observations (water-cell transmissions of 33 to 35 per cent., October 20th to 22nd and 28 to 30 per cent. in November), which showed that the temperature of the south polar region had risen to perhaps 10 to 15° C.

While such a temperature rise may seem preposterous, it is well to remember that at the time when the last observations were made the south polar region of Mars had been exposed to the Sun continuously for about six months; and hence a considerable rise in temperature should be expected.

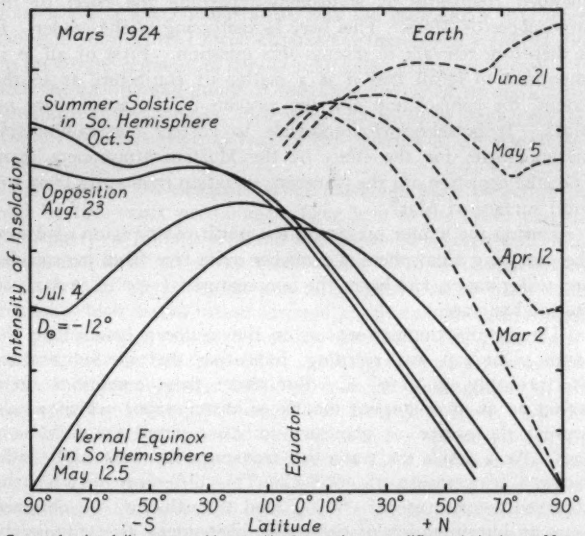
These results are so unusual that it is important to consider the seasonal changes in insolation on this planet. In Fig. 6 are illustrated some calculations of the daily amount of solar radiation received per unit area at different latitudes on Mars, taking into consideration the changes in the distance of the planet from the Sun.

The first conspicuous feature of these curves is that the intensity of the solar radiation incident upon the equatorial belt is closely the same throughout the whole series of observations extending over a period of several months. This explains the constancy of the temperatures about the centre of disc, as shown in Fig. 5. The observations confirm the calculations which show that the decreased normal intensity at the equator, due to the

southern declination of the Sun at the time of the solstice, appears to be almost exactly compensated by the increased intensity resulting from the closer approach to the Sun.

The curves show a marked increase in the daily insolation on the south polar region in passing from the Martian vernal equinox in May to summer solstice, on October 5th. This does

FIG. 6.



Curves showing daily amount of heat received per unit area at different latitudes on Mars, also on the Earth (ordinates are not to same scale).

not appear to have produced as marked a rise in temperature as one might perhaps expect. But this may be owing to the melting of the polar cup which retarded the temperature rise, and especially owing to the presence of an atmosphere, clouds and mist which will be mentioned presently. The presence of clouds has been observed frequently by Lowell and others; and only recently van Biesbroeck [69] has described a remarkable luminous extension, more than 1000 miles in length, at the terminator of Mars. This phenomenon had the appearance of an extended

[69] VAN BIESBROECK: *Pop. Astron.*, **32**, p. 589, 1924.

high cloud or fog which was illuminated in the morning sky before the subjacent territory was fully illuminated and was dissipated by the heat of the Sun as it rotated into daylight.

4. EFFECT OF THE ATMOSPHERE UPON THE TEMPERATURE ESTIMATES OF THE SURFACE OF MARS.

In the foregoing pages the temperature estimates have been qualified frequently by statements regarding the effect of the atmosphere of Mars. This may be confusing to the reader. It is therefore relevant to discuss this question. First of all, it is important to recall that it is a matter of conjecture as to the extent, the composition and the amount of the atmosphere on Mars. It is therefore impossible to correct our radiometric measurements for the effect of the Martian atmosphere upon (*i.e.*, the depletion of) the planetary radiation emanating from the solid surface of Mars.

During the winter season on the north polar region of Mars, the overlying atmosphere is probably quite free from ice spicules and water vapor, and hence the temperature of −70° C. relates to the solid surface.

During the summer season on the southern hemisphere the south polar cap was receding, indicating that its temperature was probably up to 0° C. But under these conditions there would be an overhanging mantle of water vapor which would prevent the escape of planetary radiation from the solid surface. As a result the water-cell transmissions were high, indicating a temperature of −60° C. This difference between the observed temperature of −60° C. and the value, 0° C., obtained from an interpretation of the visible phenomena (*e.g.*, diminishing ice cap) is not an inconsistency but a remarkable verification of the presence of an atmosphere containing a mantle of ice spicules, or water vapor, which prevents the escape of planetary radiation from the solid surface.

As mentioned in an earlier part of this paper, the presence of clouds on Mars is a well-recognized phenomenon, and in some cases they have appeared to be dust clouds [70] instead of water vapor. At times the surface of the planet seems veiled, as if the atmosphere of Mars were in itself hazy.[71]

[70] *Lowell Obs. Bull., No. 1*, 1903.

[71] HAMILTON: *Lowell Obs. Bull., No. 82*, 1918.

The occurrence of frost deposits on Mars is also recognized. In a paper on the presence of autumnal frosts in the south polar region of Mars, Lowell [72] gives data showing that the morning frost lasted longer as the Martian season progressed later into the autumn; remaining in view till two hours after sunrise in November and almost five hours after sunrise in December.

In view of the fact that our measurements show that the bright areas are at a lower temperature than the dark areas, it is interesting to record that Lowell observed [73] that frosts appeared first on the bright regions, as they should if the areas are deserts. In both the coming and going of the snow and frost the dark areas remained visible longest, indicating the presence of vegetation. These conditions seem to require the presence of an atmosphere on Mars.

Because of the clearness of the markings when viewed at the edge of the planet, astronomers have held to the belief that the atmosphere of Mars is extremely tenuous and transparent. This interpretation is subject to qualification. For it is well known that on clear days one can see mountains fifty or more miles distant, which means vision through an air-column several times the total mass viewed in the vertical direction. But vision in the vertical direction is hampered by inhomogeneity in the water content of the atmosphere. The most recent photographs of the atmosphere of Mars, obtained by Wright,[74] show that this atmosphere extends perhaps 120 miles above the surface of the planet. Under the Earth's gravitational force this would be compressed to forty-five miles. The effective thickness of the Earth's atmosphere is estimated to be about fifty miles. On this basis it appears that the amount of atmosphere per unit surface area on Mars is quite appreciable. But with much less water on Mars, and the most of this congealed in the polar regions, it is evident that its distribution in the atmosphere cannot obstruct vision as obtains on this Earth. Nevertheless the greater mass of water vapor or ice spicules in the polar regions would prevent the escape of planetary radiation, upon which our temperature estimates are based.

While these observations were in progress, it seemed to be

[72] *Lowell Obs. Bull., No. 71*, 1911.
[73] *Lowell Obs. Bull., No. 71.*
[74] WRIGHT: *Publ. Astronom. Soc. Pacific*, **36**, p. 239, 1924.

quite an achievement to be able to differentiate between the temperature conditions of the bright and the dark regions, the polar caps, etc.; and it was tacitly assumed that, owing to the presence of Martian atmosphere, the surface temperatures of the east and west limbs of the planet were higher than the observed values.

Now that the measurements are completed and there is time for considering their significance, the demand has arisen for greater refinements in estimating temperatures than the original observations seem to justify.

Until we obtain data on the effect of the Martian atmosphere it does not seem desirable to attempt to specify more exact temperatures, especially at the poles and the limbs of the planet.

V. PLANETARY TEMPERATURES.

In his theoretical investigation of the radiation from the solar system, assuming that the planets are similar to the Earth, Poynting [75] calculated the following temperatures: Mercury, 196° C.; Venus, 69° C.; Earth, 17° C.; Mars, 38° C. He omitted Jupiter and Saturn in view of the probability that they radiated heat of their own in considerable proportion.

Under the present caption are assembled all of the available radiometric data on this subject. When no specific references are given, the subject-matter has already been cited in the preceding part of this paper.

1. MERCURY.

Pettit and Nicholson found that the water-cell transmission of the radiation from Mercury was practically the same as that of the Moon. The planetary radiation per unit area from Mercury was found to be nearly the same as from the Moon, and the conclusion arrived at is that the surface temperature of these two bodies cannot be greatly different.

From our observations and temperature calibrations of the Moon, temperatures of from 75° to 100° C. may be inferred for the irradiated side of Mars. The reason that the temperature of the irradiated surface of Mercury is not much different from the Moon may be owing to its rapid rotation.

[75] POYNTING: *Phil. Trans. Roy. Soc.*, 202, A 525, 1903; *Jahrbuch der Radioaktivität u. Elektronik*, 2, 42, 1905.

2. VENUS.

From our water-cell transmissions of 1922, Menzel calculated an effective noonday temperature of 50° C. for the surface of Venus. As already mentioned, the spectral radiation components indicate a high selective emission, over 60 per cent. being of wavelengths 8 to 12.5μ. A temperature calculation based on the ratio of the spectral components of the planetary radiation leads to absurdly high values. For the same reasons it is questionable whether our water-cell transmission should be used for calculating the temperature of the surface of Venus, using the fourth-power law of total radiation.

It is instructive to obtain the temperature of the stratosphere of Venus from the water-cell transmission (68.4 per cent.) and the calibration curve in Fig. 2. This gives a temperature of −60° C. (probably higher if we take into consideration the solar distance), which is interesting in view of our knowledge of the temperature of the Earth's stratosphere which is known to be down to −70° C., and may be still lower on the outer boundary.

While some of the planetary radiation evidently emanates from the outer atmosphere, causing the high selectivity of the spectral component at 8 to 12.5μ, no doubt some of the planetary radiation emanates from the interior. If this is admitted then it seems permissible to compare it with the planetary (nocturnal) radiation that may escape through the Earth's atmosphere. At any rate, it indicates the possibility of nocturnal radiation escaping through the Earth's stratosphere into space, which question arose in assigning a temperature to the effective radiating layer of the Earth's atmosphere.

The observation of an intense planetary radiation from the dark part of the disc raises the question whether or not this is owing to a rapid rotation of the planet. If the period of rotation is long (225 days) then it seems necessary to assume that the surface of Venus is still quite warm; although the highly selective condition of the planetary radiation at 8 to 12μ may perhaps be interpreted as owing to radiation of the hot gases convected from the illuminated over the dark part of the planetary surface. However, since this involves distances of 800 to 1000 miles over the surface, it seems difficult to reconcile this assumption with the radiative properties of the gases which

probably constitute the atmosphere of Venus. It seems more plausible to assume that the planet rotates on its axis.

As already mentioned, an interesting and important observation is that the intensity of the radiation emitted from near the south cusp of Venus in the present position of the planet—both for the dark and the illuminated regions—is greater than that emanating from corresponding points near the north cusp. This may be owing to differences in the surface conditions as previously observed on Mars. Then, again, it suggests an effect of insolation due to inclination of the axis of rotation to the Sun, analogous to seasonal changes on Mars and the Earth. Further radiometric observations, at different presentations of the planet's surface to the Earth, will be required to test this question. If this is seasonal, then it should be possible to establish the position of the axis of rotation of Venus.

3. MARS.

In a recent discussion of climatic conditions on Mars, inferred from phenomena generally observed on the planet, Pickering [76] estimated the mean annual temperature at 20° F. as compared with the mean annual temperature of the Earth of 59° F. (15° C.). At night the Martian temperature is below 32° F. (0° C.), and at noon it is, perhaps, 60 to 70° F. (15 to 20° C.). These figures are arrived at from the appearance and disappearance of snow and frost during the course of the Martian day, and from the fact that snow is never seen on the equator at Martian noon. This is in agreement with the views held by Lowell and others.

In the foregoing section of this paper it was shown that under a noonday sun the temperature of the equatorial region (the apparent centre of the disc) of Mars ranges from 5° C. for the bright regions to 20° C. for the adjacent dark regions. When there was no phase the temperature of the east limb was down to −45° C. and the temperature of the west limb was 0° C. The temperature of the irradiated north polar region, during the winter season, was down to −75° C. or perhaps even lower. At the same time, when there was (early) summer on the southern hemisphere the temperature of the irradiated south polar region, as viewed through the overhanging mantle, was −60° C. The

[76] PICKERING: *Pop. Astron.*, 30, p. 410, 1922.

temperature of the solid surface was probably 0° C.—melting snow and ice. In the late Martian summer (solstice, October 5th) the water-cell transmissions dropped rapidly to 30 per cent., or less, indicating a temperature of perhaps 10 to 15° C. The temperature of the night side of Mars is no doubt still lower than that observed on the irradiated north polar region, probably below −70° C.

An interesting deduction from these observations is the great variation in diurnal temperature on the surface of Mars as compared with the Earth. For example, at opposition the temperature at sunrise was −45° C., at noonday 20° C. and at sunset 0° C.

Another interesting feature of these measurements was the observations of slight variations of the temperature of the north polar region from night to night. Usually there was no white polar cap visible. However, sometimes a white frosty outline was apparent, which no doubt affected the measurements, producing lower temperatures.

4. JUPITER.

The water-cell transmissions (Table III) of Jupiter range from 73 to 75 per cent., which is practically the same as that of direct solar radiation. The planetary radiation is principally of wave-lengths 8 to 12.5μ which may be attributed principally to selective emission (at 10.5μ) of CO_2 and ozone in the outer atmosphere. The water-cell transmissions indicate that the temperature of the stratosphere of Jupiter is below −70° C. (−100° C. if we adopt the dotted calibration curve in Fig. 2).

Pettit and Nicholson have found water-cell transmissions up to 78 per cent., indicating a temperature of −75° C., while Menzel's calculations indicate a temperature of −110° C.

From the foregoing comparisons it appears that a reasonable estimate of the upper limiting temperature of the outer atmosphere of Jupiter is −75° C. This is much higher than can be explained on the basis of heating by solar radiation and is probably attributable to a warm interior with a stratosphere having a temperature not unlike that of the terrestrial stratosphere.

5. SATURN.

Menzel's calculations indicate a temperature of −110° C. for the ball of Saturn. It is to be noticed, however, that owing to the highly selective emission of the spectral radiation components

(similar to that of Jupiter, Table III) the method of calculation by using the water-cell transmissions in the fourth-power law of total radiation of a black body does not seem applicable.

Pettit and Nicholson's water-cell transmissions are above 76 per cent. (practically the same as for Jupiter), indicating a temperature below –70° C.

Contrary to the measurements of Pettit and Nicholson, all our observations of 1914, 1922 and 1924, on the ball of Saturn, are consistent in showing a lower water-cell transmission than that observed on Jupiter. The values range from 67 to 68 per cent., indicating a temperature of about –65° C. (–85° C. if we accept the dotted calibration curve in Fig. 2). The rings are at a somewhat lower temperature. As noticed in the case of Jupiter, the temperature of Saturn is higher than would be expected on the basis of solar heating and is probably attributable to a fairly warm condition of the interior.

6. URANUS.

Within the experimental errors of observation the water-cell transmission of the radiation of Uranus is practically that of the direct solar radiation. The temperature is therefore at least as low as that of the effective radiating layer of the Earth's atmosphere, which in this investigation was taken at –70° C. The temperature of the effective radiating layer of gases forming the outer envelope of Uranus is not higher than –75° C.; though it is a mere conjecture as to how much lower the temperature may be on this planet.

7. THE MOON.

The calculated temperatures of the full Moon range from 110° C. by Dietzius to 125° C. by Menzel. Very's direct measurements indicated temperatures up to 175° C. As already mentioned, these temperature estimates form the basis of one of our methods of obtaining the temperature of Mars.

In the foregoing part of this paper it was recorded that no radiation was observed from the unilluminated part of the disc in comparison with that of the sky. On the basis that the isothermal layer behaves like an opaque screen, this would indicate a temperature of –70° C.

This would be an upper limit in escaping detection radiometrically. For it is possible for radiation of wave-lengths 8 to 15μ

to pass through the Earth's atmosphere into space, which is generally considered to be at a very low temperature, perhaps down to −273° C. Since the thermocouples were probably emitting radiation of wave-lengths 8 to 15μ into space, and since no deflection was observed on setting our receiver on the unilluminated part of the disc, it would appear that the lunar temperature was down close to that of interstellar space. At these low temperatures the radiation of wave-lengths 8 to 15μ is small relative to the total radiation of all wave-lengths emitted, but not transmitted by the atmosphere. Hence, it might escape detection. We can, therefore, say that the temperature was not higher than −70° C. Very estimated the night temperature of the Moon to be lower than −200° C. In this connection it is interesting to note that the most recent calculations, by Dietzius, gave a temperature of −79° C. immediately preceding lunar sunrise.

In concluding this discussion of planetary temperatures, it is relevant to consider the significance of the highly selective condition of the spectral components of the radiation from the planets having dense atmospheres. In this case the planetary radiation is no doubt a composite of the radiation of wave-lengths 8 to 15μ, which emanates from the heated interior and is transmitted by the surrounding atmosphere, plus the narrow spectral band of radiation, principally of wave-length 10.5μ, emitted by the heated ozone (if present) which is on the outer boundary of the atmosphere.

From Table III, it appears that for Jupiter and Saturn, the ratio of the spectral components is $A:B=3$, and for Venus the ratio of $A:B=2$. If the planetary radiation from Jupiter and Saturn emanated entirely from the interior then, since the insolation is low, the temperature of the interior should be low, and the ratio should be less than unity, as calculated for non-selective radiation.

Similarly, since the insolation on Venus is many times greater than that of Jupiter, the planetary radiation from the interior should be greater and the ratio of the spectral components should be smaller than that of Jupiter and Saturn. This is in agreement with the observations. In other words, the selective emission of CO_2 and ozone from the outside of the atmosphere of Venus, combined with the radiation transmitted from the interior, produce a smaller ratio than observed on Jupiter and Saturn. If practically all of the planetary radiation from Venus were from the

outer atmosphere, then the ratio of the spectral components should be higher, as observed on Jupiter and Saturn. From this it appears to be impractical to apply the radiation laws to the spectral components of the highly selective planetary radiation from the planets having dense atmospheres.

VI. SUMMARY.

The object of the present paper is (1) to describe further measurements of the radiation emitted by planets; (2) to give an account of some preliminary attempts at separating this planetary radiation into spectral components; and (3) to give estimates of planetary temperatures.

By means of a series of transmission screens of water, quartz, glass, and fluorite, the radiation emanating from the planets, *e.g.*, Mars, was separated into spectral components and the radiation intensities determined in the spectral regions of 0.3 to 1.4μ, 1.4 to 4.1μ, 4.1 to 8μ, 8 to 12.5μ, and 12.5 to 15μ.

In this manner, it is possible to determine the shape of the spectral energy curve of that part of the planetary radiation which is transmitted by our atmosphere and thereby form an estimate of the temperature of the effective radiating surface of the planet. This appears to be a new method which, heretofore, has not been used.

Radiometric measurements were made on Venus, Mars, Jupiter, Saturn, Uranus, the Moon and on terrestrial sources. The results obtained verify our previous observations of 1921, showing that the planetary radiation emanating from Jupiter and from Saturn, and transmitted by our atmosphere, is very small, while the planetary radiation from Venus, Mars and the Moon, is, relatively, very intense.

The outstanding features of this investigation are the results of the measurements on selected regions on the surface of Venus, and of Mars. The measurements on Venus were made when the bright phase was a narrow crescent. Under these conditions the dark part was found to emit an intense planetary radiation amounting (per unit area) to 10 per cent. of the total radiation from the bright crescent. This raises the question whether the radiation from the dark side of the planet is owing to a short period of rotation. The dark and the bright regions near the south cusp were found to be hotter than corresponding points

near the north cusp, just as was previously observed on Mars. Whether this is owing to physical differences of the surface, or owing to different climatic conditions, as a result of a periodic variation in the inclination of the axis of rotation to the Sun, analogous to the seasonal changes on Mars and on the Earth, remains to be determined. If this temperature variation is seasonal, then it may be possible to determine the position of the axis of rotation.

Radiometric measurements were made on Mars on twenty-four nights, under a wide range of instrumental and meteorological conditions. These measurements show that under a noonday sun, the bright equatorial regions of Mars are cooler than the adjoining dark regions; that the sunrise side of the planet is at a lower temperature than the side exposed to the afternoon sun; and that the polar regions are cold—emitting no planetary radiation, and having low temperatures.

An estimate of the temperature of the irradiated surface of Mars was obtained by four methods, as follows: (1) By comparison with terrestrial conditions, Martian temperatures similar to those found on the Earth were inferred; (2) by direct comparison of the spectral components of the planetary radiation from Mars and the Moon, noonday temperatures were obtained ranging from 5° C. for the bright equatorial region to 20° C. for the adjacent dark regions; (3) by comparison of the observed spectral components of the planetary radiation from Mars with similar data calculated from the laws of spectral radiation of a black body, temperatures were obtained ranging from −15° C. for the bright equatorial regions to 18° C. for the adjoining dark regions; and (4) by applying the fourth-power law of total radiation to the water-cell transmissions of isolated regions, temperatures were calculated, ranging from −5° C. for the bright regions to +10° C. (= 20° C. when corrected on the basis of non-black-body radiation).

At opposition, when there was no phase on Mars, the noonday temperature of the bright regions on the equator was 5° C. and that of the adjacent dark regions 20° C. At the same time the east limb (sunrise) edge was −45° C. and the west limb (sunset) was 0° C. The temperature of the illuminated north polar region, where winter prevailed was down to −75° C.; and, with summer conditions on the southern hemisphere, the tem-

perature of the south polar region, as viewed through the atmospheric mantle, was –60° C., and probably 0° C. for the solid surface. In late summer the temperature of the south pole was up to 12° C. or even higher. The temperature of the night side of Mars is probably below –70° C. This great variation in diurnal temperatures indicates a rare atmosphere.

The average of all the measurements, on the equatorial belt of Mars, at perihelion, gives a noonday black-body temperature of 8° C. (true temperature 15 to 20° C.) as compared with 16° C., obtained by direct calibration against the Moon. The integrated temperature of the whole disc is –30° C. in July.

As a whole, these temperature estimates are in harmony with visual observations on Mars. The measurements show that the noonday temperature of the equatorial surface of Mars at perihelion is not unlike that of a cool bright day on this Earth, with temperatures ranging from 5° to 15° C., or 40° F. to 60° F.

The temperature estimates of the other planets are as follows: Mercury, 75 to 100° C.; the upper limiting temperatures of the outer atmospheres of Venus, Jupiter, Saturn and Uranus, –60° (probably a low value), –75°, –65° and –75° C., respectively; and the unilluminated face of the Moon, –75° C. to –200° C.

The planetary radiation from Venus and Jupiter seems to be highly selective, and concentrated principally in the spectral component at 8 to 12.5μ. As a result, the temperatures, inferred from the ratios of spectral components, are so inordinately high that this method of analysis seems impracticable in assigning temperatures, though useful in demonstrating selective emission.

Uranus does not appear to emit planetary radiation which is in agreement with other astronomical data.

Among the subsidiary investigations (to be given in the complete paper) were measurements of the radiation from terrestrial sources, such as buildings and distant mountain peaks under solar irradiation, and in connection with the theory of radiation exchanges, planetary radiation and planetary temperatures are discussed.

IN A note published in *Nature*, December 20, 1924, MR. T. F. WALL, of the University of Sheffield, states that he has obtained a magnetic field of 1,400,000 gauss and expresses his confidence in producing a field of the incredible strength of 10,000,000 gauss.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

A NEW METHOD FOR PHOTOGRAPHIC SPECTROPHOTOMETRY.[1]

By L. A. Jones.

THE method described is designed to eliminate many of the errors which frequently occur in this type of work. A photographic plate is exposed behind a grid composed of narrow opaque strips in contact with the emulsion surface of the plate and lying parallel to the direction of the entrance slit of the spectrograph. The spaces between the consecutive elements of the grid are equal in width to the opaque elements. In this way a series of parallel strips of the photographic plate is exposed, after which by moving the plate laterally by the distance equal to the width of the grid strip, the remainder of the plate may be exposed. The first exposure is made with a photographic plate moving at a uniform linear velocity past a slit lying in the focal plane of the spectrum and in a direction perpendicular to the slit of the instrument. During this exposure the intensity of the light is decreased logarithmically by means of a diaphragm operated by a cam of suitable shape. The photographic plate is then shifted laterally so that the exposed areas are protected and a second exposure given with the exposure gradient in the opposite direction. The absorbing solution or filter under test is placed in position during one of the exposures. In this way a series of interspaced exposed strips is obtained which, upon development, result in graduated densities. By measuring the distance from the edge of the plate at which equality of density on a pair of adjacent strips occurs, the absorption of any unknown material for radiation of various wave-lengths can be determined. In this way errors due to intermittency, failure of the reciprocity law, local variations in

* Communicated by the Director.

[1] Communication No. 221 from the Research Laboratories of the Eastman Kodak Company, and published in *J. Opt. Soc. Amer.*, 10:561, 1925.

sensitivity, and variations in extent of development are eliminated. Furthermore, the necessity of measuring absolute values of density is avoided.

THE PLASTICITY OF CELLULOSE IN CUPRAMMONIUM HYDROXIDE.[1]

By E. K. Carver and H. Folts.

BY MEANS of an improved Bingham plastometer, curves were obtained of the plasticity of cellulose in cuprammonium hydroxide. The law of Joyner, that the logarithm of "viscosity" is proportional to concentration, appeared to hold fairly well at different rates of flow, although the "viscosity" of a given solution varied more than ten-fold, depending on the rate of flow.

EFFECT OF NITROGEN AND CARBON DIOXIDE DILUTIONS ON THE EXPLOSIVE LIMITS OF ACETONE AND METHYL ALCOHOL AND THEIR MIXTURES.[2]

By H. Crouch and E. K. Carver.

THE maximum and minimum concentrations at which explosions will occur for acetone, methyl alcohol, and mixtures of the two, with air containing varying amounts of oxygen and carbon dioxide have been determined. A two-litre glass flask was used as the explosion chamber. The gases were ignited by means of a bit of nitro cotton, which in turn was ignited by an induction spark.

Synthetic Methanol.—The industrial production of synthetic methanol (wood alcohol) is described by CHARLES LORMAND (*Ind. Eng. Chem.*, 1925, xvii, 430–432). Carbon monoxide and hydrogen are mixed in the ratio of one volume of the former to two volumes of the latter. The mixture is subjected to a pressure of several hundred atmospheres, then forced over a suitable catalyst at a temperature of 250° to 350° C. Powdered copper plus either zinc oxide or zinc dust, chromates, vanadates, molybdates, tungstates, and manganates may be used as catalysts. Several tons of methanol may be manufactured by this process daily, at a cost of 18 to 26 cents per gallon. J. S. H.

[1] Communicatinon No. 226 from the Research Laboratories of the Eastman Kodak Company and published in *J. Am. Chem. Soc.*, 47 : 1430, 1925.

[2] Communication No. 230 from the Research Laboratories of the Eastman Kodak Company and published in *Ind. Eng. Chem.*, 17 : 641, 1925.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

INDUSTRIAL APPLICATIONS OF INVERTASE.[1]

By H. S. Paine, C. F. Walton, Jr., and M. S. Badollet.

[ABSTRACT.]

THE ability to undergo hydrolysis, with transformation into invert sugar, is one of the important properties of sucrose and plays an essential part in many commercial methods of utilization of this sugar. The enzyme invertase is more suitable than an acid as a catalyst in the case of saccharine products which show a pronounced buffer effect toward added acid and which have a flavor adversely influenced by the quantity of acid required. The use of invertase as a catalyst for sucrose inversion has been successfully industrialized for several commercial products in which sucrose is the principal saccharine constituent. Procedures for invertase inversion of sucrose in golden syrup, cane and sorghum syrups, maple syrup and maple cream, and fondant types of confectionery have been devised.

OPTICAL ROTATION AND ATOMIC DIMENSION. IV.[2]

By D. H. Brauns.

[ABSTRACT.]

A REVISION of the specific rotation values reported in the literature has been made for chloro-, bromo- and iodo-tetra-acetyl-glucose and for chloro- and bromo-triacetyl-xylose. The corrected values, as contrasted with the values given in the literature, show a markedly better agreement between the ratio of the difference in specific rotation, Cl-F, Br-Cl and I-Br, and the ratio of the differences of atomic diameters recorded by Bragg.

It may be inferred from the relation stated above that the rotation of the pure iodo-triacetyl-l-arabinose is about 4° higher than the measured rotation (+339) of this unstable compound.

The determination of specific rotations of sets of derivatives

* Communicated by the Chief of the Bureau.

[1] Published in *Ind. Eng. Chem.*, 17 (May, 1925) : 445.

[2] Published in *J. Am. Chem. Soc.*, 47 (May, 1925) : 1280.

the same as, or similar to, those investigated, may furnish a new method for ascertaining atomic dimension values.

OPTICAL ROTATION AND ATOMIC DIMENSION. V.[3]

By D. H. Brauns.

[ABSTRACT.]

Two classes of asymmetric compounds containing substituted halogens are recognized: (1) A class in which the halogens are directly attached to the asymmetric carbon atom, where every molecule acts in the ratio of its weight, yielding quantities of activity that increase with the atomic dimensions of the halogens; (2) a class in which the halogens modify an asymmetric group attached to the asymmetric carbon atom, where every molecule acts as a unit for yielding the result obtained in the first class.

It has not yet been determined whether an abrupt or a gradual change from Class 1 to Class 2 exists when a chain of one or more atoms is introduced between asymmetric carbon and halogen. The behavior of the compounds in Class 1, however, is unexpected, and this class will first be investigated for other kinds of derivatives.

The outlook for including the hydrogen derivatives in the comparison is favorable, but such inclusion must await further experimental data.

The specific rotations of halogen derivatives of salicin and their pentacetates have been measured, and the properties and composition of α-fluoro, chloro- and bromo-acetyl-tetra-acetyl-glucose determined.

A METHOD FOR THE ESTIMATION OF HYDROGEN SULPHIDE IN PROTEINACEOUS FOOD PRODUCTS.[4]

By L. H. Almy.

[ABSTRACT.]

A METHOD for the estimation of hydrogen sulphide in food products, which comprises the following features, has been developed: (1) Removal of sulphide sulphur from the material by a current of carbon dioxide acting on an aqueous acidified suspension of the product; (2) absorption of the evolved hydrogen

[3] Published in *J. Am. Chem. Soc.*, 47 (May, 1925): 1285.
[4] Published in *J. Am. Chem. Soc.*, 47 (May, 1925): 1381.

sulphide in dilute zinc acetate solution; (3) evaluation of the sulphide content of the absorbing solution, by a comparison with standards of the "methylene blue" color produced by interaction of the hydrogen sulphide with p-amino-dimethylaniline, hydrochloric acid and ferric chloride, according to the well-known Lauth's reaction.

Analyses of beef, pork and fish showed that hydrogen sulphide was formed progressively during the putrefaction of these products.

THE CHEMICAL COMPOSITION OF CALIFORNIA OLIVE OIL.[8]

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

THE oil investigated was pressed in a commercial plant from Mission olives (crop of 1923), grown in Butte County, Calif. It was washed with water and filtered at the plant. It had a greenish color and a fine flavor. Its physical and chemical characteristics were determined with the following results:

Specific gravity 25/15	0.9119
Refractive index at 20° C.	1.4690
Acid value	1.5
Iodine number (Hanus)	85.1
Saponification value	190.6
Unsaponifiable matter (per cent.)	1.0
Acetyl value	11.2
Saturated acids (per cent.)	8.9
Unsaturated acids (per cent.)	85.2

The chemical composition of this olive oil has been determined as follows:

	Acid.	%
Glycerides of	Oleic	84.4
	Linolic	4.6
	Myristic	trace
	Palmitic	6.9
	Stearic	2.3
	Arachidic	0.1
Unsaponifiable matter		1.0

Stearic acid was found to constitute approximately 25 per cent. of the saturated acids, and it is believed that the much discussed question of its presence or absence in olive oil has been definitely settled by this investigation.

[8] Published in *J. Oil and Fat Ind.*, **2** (April, 1925): 40.

The Fused Silica Industry.—*Nature* (March 28, 1925) takes satisfaction in the flourishing state of this rather restricted branch of manufacturing. Starting at Wallsend-on-Tyne early this century, at first it grew slowly, but the War accelerated its development, for German supplies of porcelain were cut off and recognition came of the value of silica parts in the production of nitric and sulphuric acid. Later the same material has come into use in two processes of making hydrochloric acid, and a very extensive application of fused silica for gas globes and globes for indirect lighting has been made. For this use more of the material is employed than for any other. There is also a constantly widening list of laboratory apparatus made of fused silica. A mercury condensation pump has recently appeared made completely of this substance. Operating with only 5 c.c. of mercury, it gives a vacuum of .000002 mm.

The translucency or opacity of articles made of fused silica depends not only on the purity of the raw material, but on small air bubbles included. Melted sand is very viscous and the bubbles cannot escape, but fused quartz-crystal is much less viscous. The product, translucent by reason of the bubbles, is well fitted for globes and for objects where the surface is to be glazed. The cost of production remains high because skilled labor and very carefully selected materials must be used and the type of electrical equipment used is expensive. It is predicted that a large demand for fused silica would result in a considerable lowering of the cost. G. F. S.

Dusting Orchards by Airplane. (U. S. Department of Agriculture, Clip Sheet No. 357.)—The commercial peach orchard is the latest crop to receive treatment by the airplane dusting method for controlling insect pests. According to a report received by the Bureau of Entomology of the United States Department of Agriculture from its field station at Fort Valley, Ga., this process was tried for the first time in March of this year. Airplane dusting for cotton fields has been a demonstrated success, and the outcome of this type of control for insects affecting peach trees will be awaited with interest.

It took an hour and fifty-five minutes to dust 10,000 peach trees with a mixture of arsenate of lead and hydrated lime. The time recorded included all trips to the landing field to refill the hopper. For several months the bureau representatives at the Fort Valley laboratory have been giving attention to the perfection of the technique for using airplanes in this way, with the coöperation of those who have had previous experience in the work at the boll weevil laboratory at Tallulah, La. It has been necessary to make adjustments of the feeding mechanism of the planes so that the heavy dust used for peach insect control work would be evenly distributed. A thousand acres of peach trees in Georgia will be treated by airplane during the season, under the supervision of the Fort Valley laboratory. It is expected that this work will yield valuable data on the results, cost of operation, and other points.

NOTES FROM THE U. S. BUREAU OF MINES.*

THE FORMATION OF OIL-FIELD EMULSIONS.

By D. B. Dow.

THE appearance of water in an oil field is the forerunner of various difficulties, and probably represents the greatest technical problem that the producer must face. Water conditions bear directly on the quantity of oil recovered, and the length of the life of a field. Presence of water increases the cost of operation, for example, lifting costs. On account of the corrosive action of oil-field waters on pumps and other equipment, frequent replacement of equipment is necessary. Furthermore, water may affect the marketability of the oil produced, as detrimental emulsions of water in oil ("B. S.," "cut oil," etc.) are often formed.

The writer has recently completed a study of oil-field emulsions. The factors responsible for the formation of emulsions are described in Serial 2683 and methods now utilized for dehydrating oil-field emulsions are discussed in Serial 2688.

FRICTION FACTORS FOR METAL-MINE AIRWAYS.

By G. E. McElroy and A. S. Richardson.

WE made a large number of careful determinations of the resistance to the passage of air in selected sections of airways in the metal mines of Butte, Mont. From the data obtained we compiled a table of friction factors, or coefficients of friction, that is, values of K in the generally accepted formula for air flow of $P = \frac{KSV^2}{A}$ or $H = \frac{KSV^2}{A \times 5.2}$, where, in units customary to mining practice:

P = total pressure loss in pounds per square foot,
H = total pressure loss in inches of water (at 60° F.),
S = total rubbing surface in square feet—$L \times P$,
L = length in feet,
P = perimeter in feet,
V = velocity in feet per minute,
A = area of cross-section in square feet, and
K = friction factor for air weighing 0.075 pound per cubic foot.

* Communicated by the Acting Director.

It was found that mine airways could be grouped into four major types of surfaces. Each of these groups is then subdivided into three classes as to degree of irregularity of surfaces, areas and alignment, and the twelve values assigned to straight clean airways of these twelve general types are the basic values upon which the table is constructed. Further details are shown in Serial 2663.

A CONVENIENT METHOD FOR DETERMINING GUM-FORMING MATERIAL IN GASOLINE.

By M. B. Cooke.

AN analytical method for the determination of the gum-forming material in gasoline has been developed by the Bureau of Mines, during a study now in progress to determine the best ways for elimination of such constituents from gasoline. This method is similar in principle to that previously described by Smith and Cooke, which involved evaporation of a sample of gasoline in a small glass dish. The evaporation was started on an actively boiling steam bath and completed in an air oven at 105° C.

In the improved method, the steam bath has been replaced by a steam-heated oven in which an inert atmosphere is maintained. Air is excluded from the oven, consequently the precision of the determination is increased. Furthermore, porcelain evaporating dishes may be used, whereas the former method was restricted to glass dishes. A more complete description will be found in Serial 2686.

METHODS OF LABORATORY GRINDING OF COKE FOR ANALYSIS.

By W. A. Selvig.

EXPERIMENTS were made at the request of the American Society for Testing Materials, as to the probable contamination of laboratory samples of coke when pulverized to pass a No. 60 sieve of the U. S. Standard Sieve Series by methods other than by ball-mills or hard-steel diamond mortars, which methods are specified in the standard methods of that Society. After pulverizing, representative samples were analyzed by the Bureau of Mines at Pittsburgh for ash content to detect any contamination of the samples by the pulverizing apparatus.

The results showed that coke samples may be pulverized to pass a No. 60 sieve for laboratory analysis by means of Abbe ball-mills with flint pebbles, roll crushers kept in good condition and with the rolls rotating at the same speed, or by impact in a hard-steel diamond mortar without any appreciable contamination from the grinding apparatus. Disc pulverizers or bucking boards are likely to contaminate the coke appreciably. Pulverizing in a hard-steel diamond mortar is tedious. Ball-mills or roll crushers appear to be the most practical methods for pulverizing coke to pass a No. 60 sieve. The experiments are fully described in Serial 2679, recently issued.

The Molecular Mechanism of Capillary Phenomena. N. K. Adam. (*Nature*, April 4, 1925.)—It is so common to explain the actions clustering around surface tension by reference to a stretched film covering the liquid that unconsciously one comes to believe in the veritable existence of such a film. With this belief issue is taken by the author: "Although any free energy resident at the surface may mathematically be considered as the product of a 'surface tension' and the area, there is no justification in this fact for including that the molecular arrangements and forces at the surface resemble those in a stretched membrane. Indeed, probably all the attempts made to explain the molecular structure of surfaces, which have assumed such a contractile mechanism, have been complete failures."

In the midst of a liquid a molecule is subject to equal attractions in all directions, while a second molecule at the surface experiences a force directed toward the main body of the liquid. This force opposes the motion of molecules toward the surface and accelerates their motion away from it, so that more molecules leave the surface than reach it. Since each molecule has dimensions, this fact perforce is followed by a reduction in the area of the surface.

A droplet of oil on a water surface usually spreads out over the surface. This effect is attributed to the surface tension of the water being greater than that of the oil. Thus the water draws the oil away from the spot where it reached the water. The author, however, regards the effect as due to an outward thrust from the oil and adduces in its support an observation made by Osborne Reynolds. When the above experiment is performed by placing oil on dusted water, the dust is moved back from the advancing oil only just in front of it and not all over the water surface as would be expected were the entire surface to contract. G. F. S.

The Structure of Radiation. E. C. STONER. (*Proc. Cambridge Phil. Soc.*, **22**, Pt. 4.)—The theory of light is at the present time in a most unhappy state. Interference and many other phenomena can be most readily explained by supposing light to be a transverse wave motion spreading out from the source. Another group of equally well-established effects is best comprehended as due to quanta, "bundles of energy" emitted by the source not continuously but at intervals. To this group belong the photo-electric phenomena and the relations between the wave-lengths of the lines in emission spectra and, in general, Bohr's theory of the atom (the importance of the work of this Danish physicist may be inferred from the fact that a certain distinguished professor of physics in an American university is learning Danish so that he may the more promptly acquaint himself with Bohr's papers, which appear first in this language and only later in the usual vehicles of science). Between these two conceptions of light there is a great gulf fixed, which so far no man is able to bridge. "Neither the wave nor the quantum hypothesis, in its present form, however, seems to offer any means of explaining the phenomena covered by the other; indeed each hypothesis seems definitely, in many cases, to rule out the possibility of the occurrence of effects which are actually observed." To those who desire to learn how serious is the incompatibility of the two views, this paper is to be recommended. The frank recognition of the mutual exclusiveness of the two hypotheses by such men as Bohr, Jeans and Lorentz, however, forms a veritable bow of promise in the cloud of uncertainty that prevails, and it can scarcely be long before some solution of the difficulty is found. G. F. S.

The Determination of the Frequency of an Alternating Current Supply by the Vibrations of Rods. G. F. C. SEARLE. (*Proc. Cambridge Phil. Soc.*, **22**, Pt. 4.)—A thin steel rod is held in a clamp so that a part projects. The end distant from the clamp is not supported. An electromagnet traversed by the alternating current is brought near to the rod and the length of the latter is adjusted until by resonance it is brought into vibration by the electromagnet. "The engines at the power station do not run at an absolutely constant speed, and it may happen that a length that gives strong resonance at one moment fails to do so shortly afterwards." The rod may be used either alone or with a magnetizing coil coaxial with it. By certain manipulations the rod can be made to respond to magnetically applied forces of either once or twice the frequency of the current. In a specific case the number of cycles determined from these two instances of resonance was 93.72 and 93.65, respectively. This paper abounds in the detailed knowledge and experimental adroitness that characterize the work of the author.

G. F. S.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, June 3, 1925.)

131 North Nineteenth Street,
Philadelphia, June 3, 1925.

Mr. Harold Calvert *in the Chair.*

The following report was presented for final action:

No. 2836: Wilson Ray Track Apparatus.

This apparatus, invented by Prof. Charles Thomson Rees Wilson, of Cambridge, England, is for the specific purpose of making visible the paths of ionizing radiations through a gas.

The announcement of the discovery of a method of making these paths visible, for the demonstration of which this apparatus was designed, was made by Professor Wilson in a paper read before the Royal Society on May 11, 1911. His brief statement of the discovery was as follows: "The tracks of individual alpha or beta particles, or of ionizing rays of any kind, through a moist gas may be made visible by condensing water upon the ions set free, a suitable form of expansion apparatus being used for the purpose."

The essential features of this expansion apparatus include a cylindrical expansion chamber, the top, sides and floor being of glass, coated inside with gelatine, the floor coating blackened with India ink. The volume of the chamber is increased by lowering the floor and diminished by raising it. The air in the chamber is kept charged with water vapor and whenever a source of alpha or beta particles is introduced into the chamber, a high intensity light source, sent through it in a horizontal direction, illuminates the tracks of these particles so that they can be seen or photographed.

The importance of the method may be summarized as due to the fact that it affords one of the very few methods which the physicist possesses for the study of individual atoms, individual electrons and individual quanta of radiation. For this reason it is believed that the method is one of permanent value.

Considering this a scientific contribution of great importance, The Franklin Institute recognizes it by the award to Professor Wilson of the Howard N. Potts Gold Medal and Certificate.

The following report was presented for first reading:

No. 2810: Chronometric Tachometer.

George A. Hoadley,
S. and A. Assistant.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, June 10, 1925.)

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LIBRARY NOTES.

PURCHASES.

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BOOK REVIEWS.

COLLEGE CHEMISTRY. By Lyman C. Newell, Boston University. vi–645 pages, 213 illustrations, 12mo. Boston, D. C. Heath and Company, 1925.

It is a very difficult task at the present time to write a textbook of elementary chemistry. The quantity and quality of the data of the science have increased of late years enormously both in extent and abstruseness. Physical chemistry has been so highly developed that it threatens to throw chemistry proper into the background or relegate chemists to the purely applied phases of the science. It is noticeable that most of the workers who are now so prominently mentioned in connection with the subjects of atomic structure, colloids, radio-activity and electro-chemistry are physicists. In the standard manuals a half century ago a brief outline of physics, especially as regards light, heat and electricity, was given with a few pages devoted to cohesion and adhesion under the title "chemical physics." The greater portion of the last-

named was devoted to an outline of Graham's work on crystalloids and colloids. Since then "colloid chemistry" has assumed the position of a special department, although Loeb in his recent writings deprecated in strong language any such specification.

The book now under review is an excellent summary of the facts and important theories of chemistry. In discussing the structure of the atom preference is given to the Lewis-Langmuir theory. It seems to the reviewer that in presenting the periodic system, Newlands is not treated exactly fairly, moreover, suggestions in regard to the significance of the numerical relations of atomic weights date back to the time of Döbereiner. Our own M. Carey Lea gave even before Newlands some interesting comparisons.

A hostile critic looking for flaws could, of course, find some upon which to expatiate, but it seems impossible in the present rush of new data to keep up to date. Thus, on page 10, it is stated that mercury cannot be further decomposed by any process "ordinarily used by chemists." Yet it is now claimed that mercury can be converted into gold by comparatively simple electrical methods. Under "sodium" it is stated that Davy gave the element the symbol Na, but the Berzelian system of symbols was not proposed until the second decade of the nineteenth century and Berzelius at first used So for sodium. A typographic error of "noon" for "room" occurs in line 10, page 22.

Beginners in chemistry will find this work comprehensive and informing as to the present views of chemists. The physico-chemical data of importance are given careful and explicit consideration and the applied phases of the science are well presented. Many interesting facts regarding the greater industries are set forth. The text is well written, the illustrations numerous and excellent, and the printing and paper of good quality. In turning over the pages it has occurred to the reviewer that some scheme for indicating the pronunciation of the names of distinguished foreign scientists might be advantageously included in elementary books. Professor Newell refers to the custom of French chemists to regard Lavoisier as the founder of modern chemistry. This should always be challenged by chemists of other nations, for while Lavoisier did much in the line of placing chemistry on a substantial basis, there were equally serviceable workers in other Continental countries and in Great Britain.

HENRY LEFFMANN.

FREEHAND DRAFTING. By Anthony E. Zipprich, Instructor of Mechanical Drawing, Mechanics Institute, New York; formerly Instructor of Industrial Drawing, Brooklyn Navy Yard Apprentice School, with introduction by Carl L. Svensen, M.E., Professor of Engineering Drawing, Ohio State University. xii + 131 pages, 6″ × 9″, cloth, 71 illustrations. New York, D. Van Nostrand Company, 1924. Price, $1.60 net.

Next to an ability to write legibly and fluently, the capacity to make an understandable sketch is of fundamental usefulness in any of the vocations of science and technology. As in learning to write a suitable program of procedure, the simplest of tools—paper and pencil—and diligence will insure proficiency. Once acquired the faculty is easily maintained.

The book here presented constitutes such a program. It opens with a short chapter on the Gothic style of lettering, a form now widely employed for the annotations of shop drawings and textbook illustrations. Proceeding by grad-

ual steps from the drawings of simple lines, circles and elementary geometric figures, the principles of representing objects by oblique orthographic projection are developed. Exercises in the sketching of simple objects, proceeding to more complex forms in properly graded difficulty, follow. The isometric method is employed in the main, but the methods of true perspective are given brief attention. The examples are on both mechanical and subjects of common occurrence and are representative and well chosen. The principles of projection, either orthographic or perspective, are only briefly considered and that is all that is necessary, the prime object is to teach dexterity of execution and to attain that, the student must practise drawing lines as directed again and again—and then again—it's like learning to write.

A minor matter open to slight criticism is the lettering of Plate 3. There the author does not appear to have adhered to his own directions with regard to the spacing of the letters, they are not sufficiently close together for a pleasing effect. Ordinary printed matter constitutes an excellent criterion for spacing. The inclination of the slanting lettering should be given, it is very easy to acquire an almost unbreakable habit of lettering with an incorrect slant. A suitable slant is 1 : 2½. LUCIEN E. PICOLET.

STATIQUE ET RÉSISTANCE DES MATÉRIAUX. Par Paul Montel, Professeur à la Sorbonne et à l'École Nationale Supérieure des Beaux-Arts. vi + 273 pages, 6″ × 9″, paper, 137 illustrations. Paris, Gauthier-Villars et Cie., 1924. Price, 30 francs.

Writers on the strength of materials have in general adhered to a strictly analytical treatment of the subject, referring to applications of the force and equilibrium polygons when applied in that connection as an alternative process. The present work is written to meet the requirements of a class of students whose training is preëminently in eye-and-hand processes and for that reason the graphical method has been employed as the fundamental framework in the development of the subject as well as in the demonstration of special theorems and solution of specific problems.

The conditions of equilibrium of external forces acting on a structural member, the reactions and stresses in truss members are uniformly determined by the method of graphical statics. Applications of the method to the determination of statical moments and moment of inertia are also demonstrated as well as constructions for arithmetical operations. This construction further is applicable to the graphic determination of definite integrals which by the introduction of the idea of vertical load is employed in the construction of the elastic curve and the evaluation of deflection. The same process leads to a demonstration of the theorem of three moments. It may be noted that this graphical method is of particular value in dealing with beams of variable section and loaded in any manner. Particular attention might be profitably directed to that feature, for that is the embarrassing problem that occasionally confronts the young engineer who has been trained only in the conventional type of text-book problems.

The only departure from graphic deduction for algebraic equations occurs

in the chapters on the theorem of three moments and in the discussion on two-hinge arches. In these the graphic method leads to complex constructions.

Illustrative examples are introduced throughout the text and an adequate number of problems is provided at the end of each chapter. The book is a thoroughly practical text, especially adapted to the requirements of engineers to whom graphic methods make a strong appeal. L. E. P.

PHYSICO-CHEMICAL EVOLUTION. By Ch. Eug. Guye, University of Geneva. Translated by J. R. Clarke, M.Sc., University of Sheffield. xii–172 pages, four diagrams, small 8vo. Printed in Great Britain, published by E. P. Dutton and Company, New York, no date. Price, $2.40.

This is largely a discussion of Carnot's principle as applied to living organisms. The subject-matter is of the advanced type and adapted to those workers in physical chemistry who have full knowledge of the latest theories and the applied mathematics thereof. The text consists of adaptations of three papers that have appeared in recent years. The first, published in 1918, was entitled "Reflections on the Classification and Unities of the Sciences." It appeared in the Geneva *Arch. d. Physiologie*. The second paper, entitled "The Evolution of Physico-chemical Phenomena and the Calculus of Probabilities," was published in *Jour. d. Chim. phys.* The third paper, "Carnot's Principle and the Physico-chemical Evolution of Living Organisms," appeared in *Arch. d. Sc. phys. et nat.*

The author pushes his investigations well into the realm of philosophy proper, for the closing pages are devoted to an essay entitled "Chance or Finalism." There is, as might be expected, an attempt to define chance, but with no greater success than has resulted from the efforts of other philosophers. As a matter of fact, Alexander Pope was right when he said, "All chance but nature which thou canst not see."

The work has no index, probably due to the bad example of the French original, and the pages are uncut, a neglect for which the publisher is to be blamed. The author is a thorough evolutionist, and the book will therefore not be admissible to some of the public schools in this country, but it will be acceptable, as noted above, to the advanced workers in the field to which it is devoted. The translation is well done. HENRY LEFFMANN.

METEORS. By Charles P. Olivier, Ph.D. xix–276 pages, illustrations, 8vo. Baltimore, Williams and Wilkins Company, 1925.

This is a timely book. It is the first general treatment of meteoric astronomy published since 1871. The book is written for the intelligent layman and for the professional astronomer.

The story is succinctly yet completely told in an inviting and charming manner. The arrangement permits one who desires to do so to read the non-technical part of the book and omit, without feeling a sense of incompleteness, the well-told chapters that contain the mathematical treatment.

The author has very conscientiously gathered material from papers, from the publications of observatories, from journals, and from observations, many of which he made himself. He has sifted the material and organized it in a most effective manner, and has answered just those questions about which one is naturally curious.

The book is rich but not overloaded with tables of statistical data. It has made accessible to students the scientific methods used to find the real height of meteors, to compute their orbits, and to establish the relations between the comets and meteor-streams. It has also discussed somewhat the theory of the manner in which meteor-streams are formed.

The question of the non-stationary meteor radians has been discussed with much completeness and fairness. This subject is one to which the amateur may make valuable observational contribution, he may learn how this may be done in the volume before us.

The author has, perhaps, contributed more to meteoric astronomy by way of observation than any other living American. He has organized the American Meteorological Society, which has made more than 30,000 observations, many of which Doctor Olivier personally made. He has directed these observations and reduced the results. The volume is such a one as could be expected from the pen of a man so rich in experience. JOHN A. MILLER.

ASSURANCES SUR LA VIE, CALCUL DES PRIMES. Par H. Galbrun, Docteur ès Sciences, Actuaire de la Banque de Paris et des Pays-Bas. 1er Fascicule du tome III du Traité du Calcul des Probabilités et de ses application, publié par M. Emile Borel (Membre de l'Institut). Paper, vi–310 pages, 6″ × 9″. Paris, Gauthier-Villars et Cie., 1924. Price, 35 francs.

Science and technology make extensive but secondary use of the theory of probability. In its application to the financial field, and particularly to the subject of life-insurance, its application is fundamental to the process. There, the theory is the indispensable instrument for the solution of the problems which arise in the development of procedure from which a suitable profit may be derived.

In this work, Doctor Galbrun has laid particular stress upon the fundamentals of the subject and on the development of general methods. Premiums on contracts with one or more individuals are always considered as probable values of a more or less complex stake on the duration of human life. That procedure has made it possible to derive rigorously the various formulas employed, to determine the degree of accuracy which they yield and, finally, in arriving at processes of numerical calculation which, though little used hitherto, are of notable simplicity. A second volume on "Theorie des Reserves Mathematique" is in preparation.

The work should prove of deep interest alike to the mathematician and to the mathematically trained actuary. L. E. P.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 200, Some Problems on the Lift and Rolling Moment of Airplane Wings. By James B. Scarborough. 16 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, ten cents.

This paper is part of the thesis submitted by the writer to Johns Hopkins University for the degree of doctor of philosophy.

It deals for the most part with the application of the airfoil and twisted wing theory to the calculation of the lift and rolling moment of airplane wings.

Most of the results arrived at are strictly true only for wings of elliptic plan form. The investigation aims to give some indications of the accuracy with which the results can be applied to the wing forms in actual use.

Report No. 201, The Effects of Shielding the Tips of Airfoils. By Elliott G. Reid. 9 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, five cents.

Tests have recently been made at the Langley Memorial Aeronautical Laboratory to ascertain whether the aerodynamic characteristics of an airfoil might be substantially improved by imposing certain limitations upon the airflow about its tips.

All of the modified forms were slightly inferior to the plain airfoil at small lift coefficients; however, by mounting thin plates, in planes perpendicular to the span, at the wing tips, the characteristics were improved throughout the range above three-tenths of the maximum lift coefficient. With this form of limitation the detrimental effect was slight; at the higher lift coefficients there resulted a considerable reduction of induced drag and, consequently, of power required for sustentation. The slope of the curve of lift *versus* angle of attack was increased.

Report No. 206, Non-metallic Diaphragms for Instruments. By H. N. Eaton and C. T. Buckingham. 44 pages, illustrations, quarto. Washington, Government Printing Office, 1925.

This report, the second of a series of reports relating to the general subject of instrument diaphragms, was prepared by the Bureau of Standards at the request of the National Advisory Committee for Aeronautics. The first report of the series was published as Technical Report No. 165, "Diaphragms for Aeronautic Instruments," and comprised an outline of historical developments and theoretical principles with a discussion of expedients for making the best use of existing diaphragms.

The present report relates entirely to non-metallic diaphragms, the use of which in certain types of pressure elements has been increasing for some time. Little, if any, information has been available, however, to aid the designer of instruments using this form of pressure element. It was to attempt to meet the need for such information that the investigation reported in this paper was undertaken.

The report describes the various materials which have been used as non-metallic diaphragms, discusses the factors which affect the performance of the diaphragms and gives the results of tests made for the purpose of investigating the effect produced by these factors. A theoretical discussion is given in which it is shown that the effective area of a non-metallic diaphragm can be computed for specified conditions and hence the pressure-deflection curve can be predicted. Curves are given to facilitate the computation of effective areas under any given condition. The theory was tested experimentally and was found accurate within about 5 per cent. Finally pressure-deflection curves are given to illustrate the control which the designer has over the shape of the curve by varying the different parts of the pressure element.

Report No. 207, Aerodynamic Characteristics of Airfoils at High Speeds. By L. J. Briggs, G. F. Hull, and H. L. Dryden. 17 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, ten cents.

This report deals with an experimental investigation of the aerodynamical characteristics of airfoils at high speeds, made at the request and with the financial assistance of the Committee. The investigation was carried out jointly by the Bureau of Standards and the Ordnance Department, U. S. A., and was made possible through the courtesy of the Lynn Works of the General Electric Company, where a large centrifugal compressor was made available for the purpose.

Lift, drag, and centre of pressure measurements were made on six airfoils of the type used by the Air Service in propeller design, at speeds ranging from 550 to 1000 feet per second. The results show a definite limit to the speed at which airfoils may efficiently be used to produce lift, the lift coefficient decreasing and the drag coefficient increasing as the speed approaches the speed of sound.

The change in the lift coefficient is large for thick airfoil sections (camber ratio 0.14 to 0.20) and for high angles of attack. The change is not marked for thin sections (camber ratio 0.10) at low angles of attack, for the speed range employed.

At high speeds the centre of pressure moves back toward the trailing edge of the airfoil as the speed increases.

The results indicate that the use of tip speeds approaching the speed of sound for propellers of customary design involves a serious loss in efficiency.

PUBLICATIONS RECEIVED.

Physico-chemical Evolution, by Ch. Eug. Guye. Translated by J. R. Clarke. xii–172 pages, illustrations, 12mo. New York, E. P. Dutton and Company, 1925. Price, $2.40.

A Textbook of Glass Technology, by F. W. Hodkin and A. Cousen. 574 pages, illustrations, plates, 8vo. New York, D. Van Nostrand Company, 1925. Price, $12.

Transmission Circuits for Telephonic Communication. Methods of Analysis and Design, by K. S. Johnson. 326 pages, diagrams, 8vo. New York, D. Van Nostrand Company, 1925. Price, $5.

Mechanical Design of Overhead Electrical Transmission Lines, by Edgar T. Painton. 274 pages, illustrations, plates, tables, 8vo. New York, D. Van Nostrand Company, 1925. Price, $6.

Abridged Scientific Publications from the Research Laboratories of the Eastman Kodak Company, Vol. viii, 1924. 155 + vi pages, illustrations, diagrams, tables, 8vo. Rochester, Eastman Kodak Company, 1925.

Ontario Department of Mines: Thirty-third Annual Report, being Volume xxxiii, Part ii, 1924. The Porcupine Gold Area, by A. G. Burrows. 112 pages, illustrations, maps, 8vo. Toronto, 1925.

Gravity: Not an Attraction, by Charles F. Johnson. 28 pages, illustrations, 8vo. Hartford, E. V. Mitchell, 1925.

The Stabilization of the Price of Wheat during the War and Its Effect upon the Returns to the Producer, by Frank M. Surface. 100 pages, diagrams, tables, quarto. Washington, United States Grain Corporation, 1925.

National Advisory Committee for Aeronautics: Technical Notes, No. 218,

The Estimation of Airplane Performance from Wind-tunnel Tests on Conventional Airplane Models, by Edward P. Warner and Shatswell Ober. 18 pages, tables, quarto. No. 219, The Comparison of Well-known and New Wing Sections Tested in the Variable Density Wind-tunnel, by George J. Higgins. 13 pages, plates, tables, quarto. Washington, Committee, 1925.

United States Department of Commerce: Scientific Paper of the Bureau of Standards, No. 505, Critical Potentials Associated with Excitation of Alkali Spark Spectra, by F. L. Mohler. 29 pages, diagrams, tables, quarto. Technologic Paper No. 280, Reclamation of Gasoline Used in Dry Cleaning, by C. C. Hubbard. 16 pages, illustrations, quarto. Circular No. 208, United States Government Master Specifications for Wire Rope. 37 pages, illustrations, plates, tables, quarto. Washington, Bureau of Standards, 1925.

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